Long term precipitation chemistry and wet deposition in a remote dry savanna site in Africa (Niger)

Corinne Galy-Lacaux, D. Laouali, L. Descroix, N. Gobron, C. Liousse

Atmos. Chem. Phys. Discuss., 8, 5761–5812, 2008
www.atmos-chem-phys-discuss.net/8/5761/2008/

Atmospheric Chemistry and Physics Discussions

Long term precipitation chemistry and wet deposition in a remote dry savanna site in Africa (Niger)

C. Galy-Lacaux[1], D. Laouali[2], L. Descroix[3], N. Gobron[4], and C. Liousse[1]

[1]Laboratoire d'Aérologie 14, Av. Edouard Belin 31 400 Toulouse, France
[2]Université Abdou Moumouni, Faculté des Sciences, Département de Physique, BP 10662, Niamey, Niger
[3]Institut de Recherche pour le Développement (IRD) Niger, Laboratoire d'étude des Transferts en Hydrologie et Environnement (UMR 5564), France
[4]European Commission – Joint research Centre, Institute for Environment and Sustainability Global Environment Monitoring Unit, TP 440, via E. Fermi, 21020 Ispra (VA), Italy

Received: 14 December 2007 – Accepted: 3 January 2008 – Published: 19 March 2008

Correspondence to: C. Galy-Lacaux (lacc@aero.obs-mip.fr)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

A long-term measurement of precipitation chemistry has been carried-out in a rural area of Banizoumbou, in the Sahel (Niger), representative of the african semi-arid savanna ecosystem. A total of 305 rainfall samples, representing 90% of the total annual rainfall, were collected with an automatic wet-only rain sampler from June 1994 to September 2005. Using ionic chromatography, pH major inorganic and organic ions were analyzed. Rainwater chemistry at the site is controlled by soil dust emissions associated to a strong terrigeneous contribution represented by SO_4^{2-}, Ca^{2+}, Carbonates, K^+ and Mg^{2+}. Calcium and carbonates represent about 40% of the total ionic charge of precipitation. The second highest contribution is nitrogenous, with annual Volume Weighed Mean (VWM) NO_3^- and NH_4^+ concentrations of 11.6 and 18.1 μeq.l^{-1}, respectively. This is the signature of ammonia sources related to animals and NO_x emissions from savannas soils rain-induced, at the beginning of the rainy season. The mean annual NH_3 and NO_2 air concentration are of 6 ppbv and 2.6 ppbv, respectively. The annual VWM precipitation concentration of sodium and chloride are both of 8.7 μeq.l^{-1} and reflects the marine signature from the monsoon humid air masses coming from the ocean. The mean pH value, calculated from the VWM of H^+, is 5.64. Acidity is neutralized by mineral dust, mainly carbonates, and/or dissolved gases such NH_3. High level of organic acidity with 8 μeq.l^{-1} and 5.2 μeq.l^{-1} of formate and acetate were found, respectively. The analysis of monthly Black Carbon emissions and FAPAR values show that both biogenic emission from vegetation and biomass burning sources could explain the organic acidity content of the precipitation. The interannual variability of the VWM concentrations around the mean (1994–2005) presents fluctuations between ±5% and ±30% mainly attributed to the variations of sources strength associated with rainfall spatio-temporal distribution. From 1994 to 2005, the total mean wet deposition flux in the Sahelian region is 60.1 mmol.m^{-2}.yr^{-1} and fluctuates around ±25%. Finally, Banizoumbou measurements, are compared to other long-term measurements of precipitation chemistry in the wet savanna of Lamto (Côte d'Ivoire) and in the forested zone

ACPD
8, 5761–5812, 2008

of Zoétélé (Cameroon). The total chemical loadings presents a strong negative gradient from the dry savanna to the forest (143.7, 100.2 to 86.6 μeq.l^{-1}), associated with the gradient of terrigeneous compounds sources. The wet deposition fluxes present an opposite gradient, with 60.0 mmol.m^{-2}.yr^{-1} in Banizoumbou, 108.6 mmol.m^{-2}.yr^{-1} in Lamto and 162.9 mmol.m^{-2}.yr^{-1} in Zoétélé, controlled by the rainfall gradient along the ecosystems transect.

1 Introduction

Atmosphere–biosphere interactions are important to understanding the biogeochemical cycles of atmospheric species that modulate the atmospheric composition. Wet- and dry- deposition of chemical species to the earth's surface play a key role in controlling the concentration of gases and aerosols in the troposphere. The chemical content of atmospheric deposition is the signature of several interacting physical and chemical mechanisms such as: emission and source amplitude; transport processes and dynamics of the atmosphere; atmospheric chemical reactions; and removal processes among others. The study of deposition thus allows for tracing the spatio-temporal evolution of atmospheric chemistry and is an important way for distinguishing between natural and anthropogenic influences. In regions where biogeochemical cycles are disturbed by human activities, atmospheric deposition can either be an important source of toxic substances or a source of nutrients for the ecosystems. Having an understanding of chemical deposition is therefore an essential aspect of a global interdisciplinary approach in order to develop a predictive capacity for the functioning ecosystems (Brimblecombe et al., 2007; Whelpdale et al., 1996).

The international program DEBITS (Deposition of Biogeochemically Important Trace Species) was initiated in 1990 as part of IGAC/IGBP (International Global Atmospheric Chemistry/ International Geosphere-Biosphere Programme) "core project" in order to study wet and dry atmospheric deposition in tropical regions (Lacaux et al., 2003, IGAC Newsletter n° 23, 2003). The DEBITS network includes about fifty measuring stations

ACPD
8, 5761–5812, 2008

evenly distributed within the tropical belt. DEBITS activities have been recently positively assessed and are continuing in the new IGAC structure (task DEBITS II, Pienaar et al., 2005; Bates et al., 2006). For tropical Africa, the IDAF (IGAC/DEBITS/AFRICA) project started in 1994. Since this date, the IDAF program, is recognized by INSU (Institut National des Sciences de l'Univers, in French) and the CNRS (Centre National de la Recherche Scientifique, in French) as a member of the Environmental Research Observatory (ORE, in French) network. The ORE IDAF has been given the mission of establishing a long-term measuring network to study the atmospheric composition and wet and dry atmospheric processes and fluxes in Africa. The IDAF program is associated to the AMMA LOP (African Monsoon Mutidisciplinary Analyses Long Observation Program, Lebel et al, 2007) program in West Central Africa and to the SAC-CLAP program (South African Climate Change Air Pollution – PICS NRF/CNRS). The main objectives of IDAF were to measure wet- and dry- deposition fluxes to identify the relative contribution of natural and anthropogenic sources and factors regulating these fluxes. The IDAF project set-up 8 monitoring sites for three types of ecosystems over West and Central Africa: dry savanna (Niger, Mali, South Africa), wet savanna (Côte d'Ivoire and Benin) and equatorial forest (Cameroon). Data from the measuring site of Banizoumbou (Niger), which represents the african dry savanna ecosystem, are analyzed here.

It is important to notice that research at the interface between biogeochemistry, ecology, and hydrology is recently receiving considerable attention, especially in arid and semi-arid environments where knowledge has been lacking (Estell et al., 2006). These ecosystems are characterized by low, erratic rainfall, high temperature, periodic droughts and low-to-no-vegetation cover. The transition from the dry season to the wet season is controlled by the monsoon mechanism. It controls many processes there and make these regions unique. All these considerations are particularly true for the african Sahelian region. Severe drought period have been registered in the 1970's and 1980's and the large meso-scale variability of the Sahelian rainfall has been studied (Lebel et al., 1992, 2003; Le Barbé and al., 2002; Messager and al., 2004; Balme et

al., 2006) and associated with hydrological processes (Goutorbe et al., 1994). Moreover, even if global modelling studies consider that natural emissions are negligible in these regions, and even if small amount of carbon and nitrogen data are available, the emissions are certainly higher and respond rapidly to environmental changes (Jaegle et al., 2005; Otter et al., 2005). The vegetation density variability in the sahel depends also on the annual rainfall variability and present a well-marked seasonal cycle (Jarlan et al., 2005; Martiny et al., 2005). At the same time the population growth (a 2-fold increase over the Sahel in the last 40 yr) remains strong, causing a severe land-use change and desertification (Rayanaut, 2001). In terms of atmospheric sources, the Sahel is identified as a strong emitter of soil dust particles and the desertification observed over the last decades explains the intensification of dust emissions in this region and the increase of the Atlantic dust export (Moulin and Chiapello, 2006).

Rainwater chemistry on arid and semi-arid environments have been reported in India (Norman et al., 2001; Satsangi et al., 1998; India) and in Israel (Herut et al., 2000). These studies analyze the precipitation chemistry for one rainy season only. In developed country, in Central and Western Europe (Puxbaum et al., 2002), in North America (Likens et al., 2001), in Central Austria (Puxbaum et al., 2002) and in Brazil (Fornero et al., 2006), studies of long-term precipitation chemistry trends have been performed as in Israel (Mamane and Gottlieb, 1995). All these studies are related to urban areas and trends are associated with anthropogenic sources evolution.

In this paper, it is proposed for the first time to study long-term (1994–2005) precipitation chemistry and wet deposition measurements at the remote dry davanna site of Banizoumbou (Niger). Synthesis for other african ecosystems such west central wet savanna and forest or south african dry savannas have been recently published (Yoboué et al., 2005; Sigha et al., 2003; Mphepya 2004, 2005). First results on the rainwater chemistry measured at Banizoumbou for the 1996 rainy season were published by Modi et al., 1996; Galy-Lacaux and Modi, 1998; Galy-Lacaux et al., 2001).

This paper is an attempt at characterizing wet deposition in the Sahelian region with the objectives to establishing linkages between the seasonal cycle and inter-annual

variability. We try first to define the main characteristics of the precipitation chemistry in the Sahelian region from a long-term monitoring of eleven year (1994–2005) of rainwater collected at Banizoumbou. Then, the determination of the mean composition of the associated wet deposition fluxes allow to investigate the influence of the potential natural or anthrogenic sources of atmospheric particles and trace gases and the influence of the annual rainfall amount to understand the chemical content of precipitation and associated wet-deposition fluxes. This work allows for the first time to analyze the inter-annual variation of precipitation chemistry and wet deposition in the dry savanna of the Sahelian region and to compare the results to those obtain from other IDAF selected sites representative of african wet savanna and equatorial humid forested ecosystems. This study contributes to the interdisciplinary research needed in arid and semiarid environment, and to better understand the cycle of nutrients deposited within natural ecosystems.

2 Experimental site

Figure 1 shows the location of the 8 IDAF sites operating in 2006 on the vegetation map of Africa (Mayaux et al., 2004). Banizoumbou (13.33° N, 2.41° E) is located in a rural and agro pastoral area of the Sahelian region of Niger, approximately 60 km eastward of Niamey in the southwest Niger. It is part of the square degree of Niamey (13–14° N; 2–3° E) included in the survey network of the HAPEX – Sahel experiment in 1992 (Goutorbe and al., 1994) dedicated to the soil-vegetation-atmosphere relations in semi-arid zone. Since the HAPEX-Sahel experiment, the Banizoumbou site has been chosen by other programs to be long term monitored as representative of the sahelian region (AERONET/Photon (National Observatory for Aerosol, http://www-loa.univ-lille1.fr/photons/), CATCH (Couplage de l'Atmosphère Tropicale et du Cycle Hydrologique, http://www.lthe.hmg.inpg.fr/catch/), ROSELT (Réseaux d'Observatoires et de Surveillance Ecologique à Long Terme), http://www.roselt-oss.org/accueil.php). Since 1994, the site of Banizoumbou is part of the IDAF network to be representative at the regional

ACPD
8, 5761–5812, 2008

scale of the semi-arid savanna ecosystem, that is, the Sahelian savanna. In 2004, the Banizoumbou site has been naturally included in the AMMA (African Monsoon Multidisciplinary Analysis) field studies of land processes to represent the Niger mesoscale site over EOP (Enhanced Observation Period) and LOP (Long Observation Period) (Lebel et al., 2007).

The IDAF Banizoumbou site is equipped to perform long-term monitoring of wet- and dry-atmospheric deposition. It includes the collection of each rainfall event (see Sect. 3) to measure the chemical composition. Since 1998, monthly gas measurements using passive samplers are performed on the site to determine surface gaseous air concentrations of NO_2, NH_3, HNO_3, O_3, and SO_2. The climate of the studied region is typically Sahelian with a dry season from October to May and a wet season from June to September. These seasons are schematically determined by the shift of the Inter Tropical Convergence Zone (ITCZ) which separate hot and dry continental air coming from the Sahara desert (Harmattan) and cooler and humid maritime air masses (monsoon) coming from the equatorial Atlantic Ocean. In January, the ITCZ is located around 5° N, corresponding to the dry season in the Sahel. In July, the ITCZ reaches about 23° N and determines the wet season in the West Africa. The maximum latitude of the ITCZ is reached in August in the Sahel. The duration of the wet season decreases from about five months in the south of the Sahel (12° N) to 3 months in the north (18° N). In Banizoumbou (13.3° N), the ITCZ in January is around 5° N and corresponds to the dry season. In May, it is located at about 15° N at the beginning of the wet season to reach a maximum in August (23° N). The annual rainfall is related to the actual duration of the rainy season, varying from 800 mm in the south to only 200 mm in the north, following a regular gradient of 1 mm km^{-1} (average 1950–1989 from Lebel et al., 1992; Lebel et al., 2003).

The Sahelian rainfall is characterized both by strong interannual variabilities and by periods of droughts such as the years 1970–1997. The Banizoumbou site presents a variability comparable to that registered in the entire Sahel from 1950 to 2002 [20° W–20° E; 10° N–20° N] (Balme et al, 2006). In this work eleven years of rain chemistry

ACPD
8, 5761–5812, 2008

at the Banizoumbou site are analyzed. The studied period goes from 1994 to 2005 (except 1995). Figure 2 displays the annual rainfall deviation to the mean observed over the period 1994–2005 at Banizoumbou. Measurements have been done in the EPSAT–Niger and AMMA CATCH observing systems. The mean annual rainfall from 1994 to 2005 at Banizoumbou is 495.1 mm (Table 1). In the time series, rainfall larger that the 1994–2005 mean are for 1994 (689 mm, or +38%) and 1998 (699 mm, or +41%). Also, rainfall deficit of more than 20% are registered during the 2000–2005 period with one exception during 2003. Similar results are observed for the entire Sahel (Balme et al., 2006).

3 Measuring procedure and chemical analysis

3.1 Rain sampling

Event sampling was carried out at the monitoring station using an automatic precipitation collector, specially designed for the IDAF network. These operate according to the following principles:

- It collects precipitation water very cleanly in a single-use polyethylene bag, avoiding aerosol deposit before the onset of the rain. A precipitation detector automatically controls the aperture of the cover, which hermetically closes the polyethylene bag. The area of rain collection is 225 cm^2.
- After each rainfall event, 50 cm^3 of the collected water are sampled in 50 ml tubes (Greiner-type). The preservation of the rainwater samples is a great problem because of the microbial degradation which could modify the chemical composition of rainwater. The method of preservation used at Banizoumbou is derived from the procedure described by Gillett and Ayers (1991). Samples are refrigerated (4°C) or frozen (−18°C) and preserved with 15 mg of thymol biocide. References

tubes filled with 15 mg of thymol and de-ionized water are analyzed by Ionic Chromatography (IC) for blank values.

From June 1994 to September 2005 (excluding 1995), 305 rainy events, representing a total rainfall amount of 4949.5 mm were collected at Banizoumbou. The total rainfall amount during the eleven years is 5485.6 mm (Table 1). The efficiency of collection (EC) is calculated for each studied year and is ranged between 76% and 99%. The mean EC equals to 90% is a confirmation of a good representativity of all the rainy seasons dataset. The annual mean rainfall amount during the period of study (1994–2005) (495.1 mm) is comparable to the annual mean collected rainfall (450 mm).

3.2 Gaseous passive samplers measurements

Measurements of monthly mean gaseous nitrogen dioxide (NO_2) and ammonia (NH_3) in the dry savanna of Banizoumbou have been performed since 1998. Gaseous NO_2 and NH_3 were collected using passive sampling techniques. These measurements are based on the property of molecular diffusion of gases and species collection on an impregnated filter specific to each pollutant. In the IDAF project, a set of passive samplers was developed at the laboratory of "Aerologie" (Toulouse). Two separate samplers are required for NH_3 and HNO_3, since different impregnated filters are needed. For NH_3, we used 1 g of citric acid diluted in 50 ml of methanol and for HNO_3 0.5 g of NaOH diluted in 50 ml of methanol. The sorption processes for these two gases occur though the following reactions:

$$NH_3(gas) + H^+ \rightarrow NH_4^+ \quad (1)$$

$$HNO_3(gas) + OH^- \rightarrow H_2O + NO_3^- \quad (2)$$

The collecting filter is placed inside the sampler and protected against mechanical impact (insect) and wind turbulence by a metallic thin stainless-steel mesh. In addition, a 1 μm teflon filter is used to exclude aerosol particles contamination by impaction

ACPD
8, 5761–5812, 2008

onto the impregnated filter. Samplers were sent to and from the field in sealed plastic containers as recommended by Ferm (1991). To prevent contamination of samplers by particles, the inlet part of the sampler is replaced by a solid cap immediately after sampling (Ferm and Rodhe, 1997). In the field, the passive gas samplers were exposed for one month periods. They were mounted under a plastic disc to avoid direct effect of wind transport and splashing from precipitation. The plastic disc was attached to a pole at 1.5 m high or more. Samplers were exposed in pairs to check reproducibility.

The ambient concentration of the gas, C_x collected by the passive sampler was calculated from the amount trapped on the sorbant filter (X in mol), the time of exposure (t in s), the diffusion coefficient of the gas (D_x) and a number of geometric characteristics of the sampler. Details of the calculations and geometry of the IDAF passive samplers are given in Galy-Lacaux et al. (2001). These samplers have been developed according the DEBITS procedures based on the work of Ferm et al. (1994). Passive samplers have been tested and validated since 1998 in the IDAF network at 6 african stations (Al Ourabi and Lacaux, 2002). The IDAF passive sampler has participated with success to a measurements program organized in different tropical and subtropical regions (Carmichaël et al., 2003).

The detection limit of the passive samplers was evaluated with the variations in the blank amounts of the impregnated filters. The blanks and the standard deviations in the blanks were 0.6 ppb for NH_3 and 0.15 ppb for HNO_3. The reproducibility between duplicates, which gives an indication of the precision of this sampling technique is about 20% and 25% for NO_2 and NH_3, respectively.

3.3 Chemical analysis

The composition of the rainwater samples was determined at the Aerologie Laboratory in Toulouse. Inorganic (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}), carbonates and organic ($HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_2O_4^{2-}$) ions are measured by ion chromatography (IC). The laboratory is equipped with a DIONEX DX500 and ICS 1000 ionic

chromatograph (IC) with two automatic samplers (AS50). The determination of anions and organic acids on the DX500 used a gradient pump (GP40), with a conductivity detector (CD20), and a DIONEX Ionpac AS-11 and AG-11 as pre column. For cations detection, the ICS 1000 in an isocratic mode with CG12A and CS12A as pre-column and column, was used. The eluents were NaOH and MSA for anions and cations, repectively. Certified ionic standards were used for IC calibration. According to the results from the laboratory since 1996 and through the international inter-comparison tests organized by WMO (World Meteorological Organization, 1997), analytical precision is estimated to be 5% or better for all the ions and represents the uncertainties on all the measurements presented in this paper.

To improve the quality of the IDAF dataset, the WMO quality criteria were applied to all the IDAF precipitation samples. These criteria were based on the calculation of the ion difference (ID) a for each sample to consider the ionic balance:

$$\text{Ion Difference \%} = 100 * ([\text{CE} - \text{AE}]/[\text{CE} + \text{AE}]) \quad (3)$$

AE is the anion sum in μeq.l^{-1} and CE is the cation sum in μeq.l^{-1}. WMO acceptance criteria are presented in WMO report (1997). In this study, the ID criteria has been applied to the 338 collected events in Banizoumbou (1994–2005). 90% of the samples are in the WMO acceptance range and were only considered to compute the database of this study, i.e. a total of 305 rainy samples.

The pH is measured with an ATI Orion 350 instrument with a combined electrode (ATI Orion model 9252) filled with KCl (4 M) and satured with AgCl. Two standard solutions (WTW) at pH 4.01 and 7.00 are used for its calibration. From the pH values, ion H^+ concentrations are calculated. The precision is of 0,01 pH unit.

4 Precipitation chemical composition and wet deposition

From the entire database and for the period 1994–2005, the mean annual chemical composition of rainfall and associated wet deposition at the Banizoumbou site, are

evaluated. Results are analyzed according to the combination of physical and chemical processes, i.e., meteorological parameters and atmospheric aerosols and gases sources strength in relation with measured precipitation chemistry. Then, the interannual trends of the precipitation chemical composition and of the associated wet deposition for the 11 yr were analyzed. The latter allows to evaluate rainfall chemistry characteristics for the african dry savanna ecosystem. The mean composition is compared to that from other IDAF sites representatives of semi-arid savannas in West and South Africa, wet savanna and forested ecosystems.

4.1 Annual Volume-Weighted Mean and Wet Deposition at the Banizoumbou site

The annual volume-weighted mean concentrations (VWM) of ionic constituents in Banizoumbou rainwater have been calculated using the following equation:

$$\mathrm{VMW}(\mu\mathrm{eq.l}^{-1}) = \sum_{i=1}^{N} c_i\, p_i / \sum_{i=1}^{N} p_i \qquad (4)$$

where c_i is the ionic concentration for each element in μeq.l^{-1}, p_i the precipitation amount for each rainy event in mm, and N the total number of samples. To calculate the mean VWM concentration of each ion over the period 1994–2005, N is considered equal to 305.

The annual Wet Deposition (WD) expressed in mmol.m^{-2}.yr^{-1} is calculated by multiplying the VWM concentrations by the annual rainfall amount. To calculate the mean WD over the 11 yr, the mean annual rainfall from 1994 to 2005 is used, i.e., 495.1 mm. Concentrations of H^+ were calculated from the measured pH values. A principal component analysis (PCA) was applied to all the rainwater measurements dataset. Correlation coefficients using the Spearman Method are presented in Table 2. These correlation coefficients between the different chemical parameters will be examined in order to determine the potential sources that influence the rainwater composition. High correlation could indicate that chemical compounds have the same origin and/or are

being advected by the same air masses.

Calculation of the annual VWM from 1994 to 2005 and the annual mean VWM for all the dataset are presented in Table 3. The calcium ion is the most abundant in Banizoumbou rainwater samples (27.3 μeq.l^{-1}). The second most dominant ion is the NH_4^+ (18.1 μeq.l^{-1}), followed in decreasing order by NO_3^-, SO_4^{2-}, Na^+, Cl^-, formate, K^+, Mg^{2+}, acetate, oxalate and propionate.

4.1.1 Marine and terrigenous contributions

To estimate the contribution of sea salt component to the precipitation composition measured in Banizoumbou, excess concentration with respect to sea salt (X*) of sulfate, chloride, potassium, calcium and magnesium using Na^+ are calculated. Reference and ratios for seawater composition are given by Keene et al. (1986). Table 4 presents different ratios : Cl^-/Na^+, SO_4^{2-}/Na^+, K^+/Na^+, Ca^{2+}/Na^+ and Mg^{2+}/Na^+ in sea water and in rain water and give the calculation of the enrichment factors (EF) of different components with respect to Na^+

$$EF = (X/Na^+)_{rain}/(X/Na^+)seawater \quad (5)$$

The annual VWM concentration of sodium and chloride are equal to the same value 8.7 μeq.l^{-1} (Table 3). A linear relationship between Na^+ and Cl^- (r=0.78) (Table 2) and a mean annual ratio of 1.00 closed to the seawater ratio (1,16) is observed (Keene et al., 1986). Back trajectories have been calculated with the Hysplit model (http://www.arl.noaa.gov/ready/hysplit4.html) to characterize dominant pathway of air masses during the wet season around the Banizoumbou site. Results clearly indicate that the monsoon air mass coming from the Guinean golf, rich in sea salt aerosols, influence the site of Banizoumbou, and explain the "marine signature" in the collected precipitation samples. Except for the (Cl^-/Na^+) ratio, the other higher ratio values suggest a non-marine origin for the components, e.g., SO_4^{2-}, Ca^{2+}, K^+ and Mg^{2+}. These components are commonly attributed to the terrigeneous source. The marine contributions for Mg^{2+}, SO_4^{2-}, Ca^{2+} and K^+ are of 33%, 12%, 2% and 3%, respectively.

ACPD
8, 5761–5812, 2008

Ca^{2+} was significantly correlated with total carbonates (r=0.84), Mg^{2+} (r=0.85) and SO_4^{2-} (r=0.83), at a confidence level higher than 1% (Table 2).This positive relationship confirms the importance of the particles coming from the desert and semiarid regions in the chemical composition of rainfall. The North african desert areas (Sahel and Sahara) are probably the most important mineral aerosol source (Kaufman et al., 2005). Due to the partial dissolution of soil dust terrigeneous components, rain in the sahelian region are highly enriched in dissolved calcium and carbonates (calcite), which may account for the major part of the ionic concentrations of rain water. Calcium and carbonates ions are the most abundant in Banizoumbou rainwater, 27.3 and 28.2 μeq.l^{-1}, respectively. In addition to calcite, dolomite, gypsum and the dissolution of other key minerals such illite, smectite, palygorskite that compose african dusts explain the enrichment of Mg^{2+}, SO_4^{2-} and K^+ (Avila et al., 1997). This result is similar to that obtained in other regions of the world such as Asia (Kulshrestha, 2005) or in the Mediterranean Basin (Lye-Pilot et al., 1986; Avila et al., 1997,1998; Pulido-Villena, 2006) affected by air masses with high loadings in soil dust particles. Taking into account the marine contribution determined before, the terrigeneous contribution is as follows: 26.9 μeq.l^{-1} (98%) for Ca^{2+}, 8.3 μeq.l^{-1} (88%) for SO_4^{2-}, 7.3 μeq.l^{-1} (97%) for K^+ and 4.6 μeq.l^{-1} (67%) for Mg^{2+}.

The sum of the potential terrigeneous ions $Ca^{2+}+Mg^{2+}+K^+ +SO_4^{2-}+HCO_3^-$ equals 75.2 μeq.l^{-1} and represents 52% of the total ionic content (about 144.1 μeq.l^{-1}) in the precipitation collected at Banizoumbou. Calcium and carbonates represent about 40% of the total ionic charge of precipitation. The terrigeneous contribution involves highest wet deposition for Ca^{2+} (6.8 mmol.m^{-2}.yr^{-1}). Wet deposition of Na^+, Cl^-, Mg^{2+}, and SO_4^{2-} are : 4.3, 4.3, 1.7, and 2.3 mmol.m^{-2}.yr^{-1}, respectively (Table 5).

To compare with results of other african sites, Table 5 gives annual VWM of terrigeneous and marine elements in selected IDAF sites representative of semi arid savannas and also present values along a transect from dry savannas to wet savanna to forest . The annual VWM concentrations of Ca^{2+} in Mali from 1997 to 2005 (Galy-Lacaux et al., 2007b) and Niger (this work, 1994–2005) is very closed and equal to 28.1 and

27.3 μeq.l^{-1}, respectively. Lower values comprised between 12.0 and 18.7 μeq.l^{-1} are found for South african dry savannas (Mphepya et al., 2005). A significant result is the terrigeneous gradient found from the dry savanna to the forest with around 27–28 μeq.l^{-1} of calcium in dry savannas of Mali and Niger, 9.5 μeq.l^{-1} in the humid savanna of Lamto in Côte d'Ivoire (Yoboué et al, 2005) and with 8.9 μeq.l^{-1} in the forested ecosystem of Cameroon (Sigha et al., 2003). The annual VWM concentrations of sulfate present the same gradient from 7 to 9 μeq.l^{-1} in the dry savannas to 5.1 μeq.l^{-1} in the forest. Sulfate VWM in South african sites have higher concentrations, 10 times higher than in remote savannas sites of West Central Africa. Mphepya et al. (2005) have clearly demonstrated the anthropogenic influence on Amersfoort located in the Highveld and the recirculation of these polluted air masses affecting the Louis Trichardt site.

Calcium atmospheric deposition fluxes in Niger and in Mali are 6.8 mmol.m^{-2}.yr^{-1} and 10.8 mmol.m^{-2}.yr^{-1}. These fluxes represent calcium deposition near or in the source region of soil dust. Ca^{2+} wet deposition fluxes in african dry savannas of Mali and Niger, calculated with low annual rainfall depth (around 500 in Niger and 800 in Mali) are of the same order of magnitude or higher than total atmospheric calcium deposition (wet+dry) reported for the North of Europe (6.1 mmol.m^{-2}.yr^{-1}) (Hultberg and Ferm, 2004) or the Pacific coast of California (5.5 mmol.m^{-2}.yr^{-1}) (Schlesinger et al., 1982).

4.1.2 Nitrogen contribution

The annual VWM concentrations of NO_3^- and NH_4^+ concentrations are 11.6 and 18.1 μeq.l^{-1}, respectively, in precipitation at Banizoumbou (Table 5). They represent after carbonates and calcium concentrations the second highest contribution to the chemical composition of rain. This result confirms the importance of the nitrogenous signature in the semi arid savanna ecosystem. It confirms also data obtained in 1989 in Kollo, Niger (9.2 μeq.l^{-1} NO_3^- and 19.1 μeq.l^{-1} NH_4^+) (Modi et al., 1995) and

in Banizoumbou in 1996 (12.3 μeq.l^{-1} NO_3^- and 12.9 μeq.l^{-1} NH_4^+ (Galy-Lacaux and Modi, 1998). At the scale of the african ecosystems, the amount of the inorganic nitrogen contained in the precipitation of dry savanna site of Banizoumbou is comparable to those measured in the dry savanna of Mali in Katibougou (NO_3^-=9.7, and NH_4^+=17.2 μeq.l^{-1}) (Table 5). South african semi-arid savannas of Louis Trichardt (LT) and Skukuza present VWM of Nitrate and Ammonium in the same order of magnitude (NO_3^-=8 to 8.1 and NH_4^+=9 to 9.7 μeq.l^{-1}) (Mphepya et al., 2005, 2006). Mphepya et al., in 2005 shows that the Amersfoort site (dry savanna near industrial sites) presents higher concentrations of nitrate (25.0 μeq.l^{-1}) and of ammonium (22.3 μeq.l^{-1}), in relation with industrial NO_x emissions.

Observing results along the transect dry savanna-wet savanna-forest, annual VWM of ammonium in the wet savanna of Lamto is comparable to that in Banizoumbou (18 μeq.l^{-1}) (Table 5). Annual nitrate VWM is lower in the wet savanna and the forest ecosystems than in the dry savannas and is in comprised between 7 and 8 μeq.l^{-1}.

The NH_4^+ component of precipitation results of the incorporation of gaseous NH_3 and particles containing NH_4^+ in clouds and rainwater. Major sources of NH_3 included bacterial decomposition of urea in animal excreta and emissions from natural or fertilized soils (Schlesinger and Hartley, 1992), savanna fires and domestic fuel wood burning (Delmas et al., 1991; Brocard et al., 1996). In the Sahelian region, the main source of ammonia must be through hydrolysis of urea from animal urine in grazed areas (Galy-Lacaux and Modi, 1998). Also, in arid and semi arid regions with alkaline soils, ammonia emissions from soils is expected to be important (Schlesinger et al., 1992). Passive samplers measurements of NH_3 have been performed in Banizoumbou since 1998. Figure 3 shows the mean monthly variations of NH_3 concentrations calculated from the monthly mean over the seven measuring years (1998–2004). The ammonia source shows for all the year a similar pattern. First rains involve high nitrogenous compounds emissions both from the soils and after biomass burning emissions. The seasonality is well defined with two maxima, one in June at the beginning of the rainy season and one in October at the beginning of the dry season. The mean annual NH_3

concentration is 6 ppbv±2 ppbv. However, monthly variability on the period 1998–2004 and associated standard deviation are higher than the deviation on the annual mean. Carmichael et al. (2003) measured from September 1999 for one year ammonia concentrations in some selected sites in Africa, Asia and South America using passive samplers. Banizoumbou was part of this WMO/GAW pilot study and measured ammonia concentrations were higher than in India and South Asia. The high ammonium content of precipitation in Niger (Banizoumbou) is clearly related to the intense source of ammonia attributed at the beginning of the wet season to soils emissions and animal excretion. Moreover, it is well known that SO_2 and NH_3 influence the acidity of precipitation. In the studied site of Banizoumbou, passive samplers measurements of SO_2 are most of the time closed to the detection limit (~0.1 ppbv). Calculation of the ratio NH_3 to SO_2 thus indicates large excess of ammonia. This ratio reverses itself in polluted areas submitted to large sulfur dioxide emissions. The ammonium wet deposition value equal to 9.0 mmol.m^{-2}.yr^{-1} for the 1994–2005 period at Banizoumbou. It is the highest deposition fluxes after calcium (Table 5). An annual VWM of ammonium of the same order of magnitude in the semi arid savanna of Mali-Katibougou and in the wet savanna of Lamto, is retrieved. For these ecosystems, the ammonium atmospheric deposition is also the highest compared to that from other compounds (13.4 and 21.2 mmol.m^{-2}.yr^{-1}).

The second nitrogenous contribution to rain chemical composition is nitrate. NO_3^- in rainfall is the final result of multiphase reaction processes of nitrogenous gases, atmospheric particles and cloud water. Nitric oxide (NO), in the non-burning season, is the major nitrogen compound released from savanna soils. Nitrogen compound flux necessary to equilibrate the Banizoumbou wet deposition of nitrate of 5.7 mmol.m^{-2}.yr^{-1} is about 2.6 ng (N) m^{-2} s^{-1}. NO emissions from savanna soils present high spatial and temporal variability linked to a large number of parameters (soil texture, soil water content, soil nitrogen status, burning, etc.) (Matson et al., 1990; Ambus and Christensen, 1994; Levine et al., 1996; Parsons et al., 1996). NO flux emission on infertile soils in semiarid savanna of South Africa of 3.5 ng N(NO) m^{-2} s^{-1} have been mea-

sured. According to Otter et al, in 2005, biogenic NO emissions from the south african savannas are equal to the amount of NO generated by biomass burning, but slightly less than those from industry. This result is in agreement with what was found in the Sahel. Original measurements of NO emission in the Sahelian savanna at Banizoumbou, where natural emissions are perturbed by grazing activities (Serça et al., 1998), showed rates of 6.09±2.64 ng N(NO) $m^{-2}.s^{-1}$. It indicates that savanna soils in Niger are strong emitters of NO. These measurements are in agreement with surface NO_2 measurements performed at the Banizoumbou site (Fig. 3). The mean annual concentration of NO_2 is of 2.6 ppbv±0.4 ppbv. The seasonal pattern of NO_2 concentration shows clearly rain-induced nitric oxide emissions from semi arid savanna soils in the Sahelian region centered around the June maxima. Surface gaseous NO_2 concentration have been coupled to NO_2 columns from the Global ozone Monitoring Experiment (GOME) by Jaegle et al., in 2004 to improve the NO_x emission budget over Africa during 2000. It can be said that regional NO_x emissions from savanna soils are therefore sufficient to equilibrate the wet deposition of nitrate measured at Banizoumbou.

The significant correlations between Mg^{2+} and NO_3^- and between Ca^{2+} and NO_3^-, both equal to 0.75, indicate potential heterogenous and multiphase chemical processes occurring between alkaline dust and gaseous nitric acid (Dentener et al., 1996; Galy-Lacaux et al., 2001). Also, the high correlation between nitrate and ammonium (r=0.74) demonstrates that the nitrogenous components are associated in common processes. This is an indication of the availability of NH_4^+, formed after ammonia inclusion in rainwater, a second neutralizing agent in the precipitation. The influence of the terrigeneous and the nitrogenous contribution has been highlighted in the rain chemistry of the Sahelian region. Their role in chemical heterogenous processes and neutralizing effects in precipitation will be investigate and discuss in Sect. 5.

4.1.3 Acidic contribution

During the study period, precipitation pH in Banizoumbou ranged from 4.9 to 7.5 with a mean VWM concentration of H^+ of 2.3 μeq.l^{-1} corresponding to a mean pH of 5.64

(Table 3). About 18% of the precipitation have an acidic pH below 5.6, which is the pH of pure water in equilibrium with atmospheric CO_2. Most of precipitation events present pH higher than 5.6 and 1% is higher than 7.0. Galy-Lacaux and Modi have already shown that precipitation chemistry in the Sahelian region is strongly affected by alkaline species acting as buffering agents (Galy and Modi, 1998; Galy-Lacaux et al., 2001). This result has been widely emphasized in other part of the world affected by desert soil dust emissions that influence rain chemistry as for example in Spain or in the Mediterranean basin (Avila, 1997, 1998; Herut et al., 2000), in Asia (Kulsherstha et al., 2003, 2005; Hu et al., 2003). Acidity is neutralized by mineral dust, mainly carbonates, and/or dissolved gases (NH_3), before entering rain chemical content.

Low annual pH value in Banizoumbou (pH 5.64) is due to the above neutralizing effects. In this study, the potential acidity is quite high if organic and mineral acidity (sulfur and nitrogen oxides) are added (34.6 μeq.l^{-1}). However, annual H^+ VWM from 1994 to 2005 is around 2.3 μeq.l^{-1} leading to a low deposition flux of 1.1 mmol.m^{-2}.yr^{-1}. The acidity in the Sahelian site of Mali is also low and comparable to Banizoumbou in Niger (pH=5.44). To the opposite, rain acidity in the dry savannas sites of South Africa is higher with pH equal to 4.35 in Amersfoort and 4.91 in Louis Trischardt. Mphepya et al. (2005, 2006) have shown that the two sites are affected by NO_x and SO_x industrial emissions of the highveld (Turner et al., 1996). Table 5 shows a strong gradient of acidity from the dry savanna, wet saavnna to the forest, with pH from 5.64, 5.16, 4.92, respectively.

Neutralization of rainwater in Banizoumbou can be evidenced by good correlations between major anions (NO_3^- and SO_4^{2-}) and major terrigeneous cations (Ca^{2+}, NH_4^+, Mg^{2+}). The regression equation fits ($Ca^{2+}+NH_4^+ + Mg^{2+} + K^+$)= 2,82 ($NO_3^- + SO_4^{2-}$) , with the regression coefficient being 0.91. A similar regression has been studied between terrigeneous cations and organic acids r=0.72. Ca^{2+} and NH_4^+ at Banizoumbou were the dominant neutralization substances.

The annual VWM of H^+ is less correlated to mineral acidity (H^+/NO_3^- r=0.46 and H^+/ SO_4^{2-} r=0.31) and more correlated to organic acids such with formate (r=0.81

ACPD
8, 5761–5812, 2008

and acetate (r=0.57). We have already discussed the high nitrogenous contribution in Banizoumbou precipitation, especially the nitrate component. A new result is that a high level of organic acidity was found. The study of the year 1996 in Banizoumbou has measured for the first time in the precipitation the original signature of organic acidity with formate VWM of 5 μeq.l^{-1} and acetate VWM of 4 μeq.l^{-1}. In this study, the annual VWM of formate over the period 1994–2005 is 8 μeq.l^{-1}, 5.2 μeq.l^{-1}for acetate and 2.0 μeq.l^{-1} for oxalate. This result is comparable to results observed in almost all the dry savannas: formate and acetate were found in the same order of magnitude. Katibougou in Mali and Louis Trichardt in South Africa have more important VWM concentrations of formate (around 10.0–11.0 μeq.l^{-1}).

The atmospheric sources of organic acids in rain have not yet been properly identified. Some proposed sources include vegetation emissions (Guenther et al., 2006) and in-cloud process (specially for formic acid) such as the hydrolysis of aldehydes followed by aqueous phase reactions with OH radicals (Chameides and Davis, 1983; Graedel and Crutzen, 1993), soil (Sanhueza and Andreae, 1991), emissions from biomass burning (Talbot et al., 1988, 1990) and also oxidation of precursor compounds in the gas phase.

Galy-Lacaux and Modi (1998), have mainly attributed the organic acidity contribution in precipitation composition to the vegetation source of Volatile Organic Carbon. Keene and Galloway (1986) have demonstrated that active plan growth periods are direct or secondary major source of organic acids in precipitation in continental regions. It seems that similar processes linked to vegetation growth can be important in the semi-arid ecosystems. In the Sahel, the response of vegetation to the first rain pulse is very active. There is a lag time between these first rains and the first vegetation cover (Jarlan et al., 2005; Martiny et al., 2005).

A long time series of space remote sensing products has been developed to estimate the Fraction of Absorbed Photosynthetically Active Radiation (FAPAR) for various optical instruments (Gobron et al., 2000, 2006, 2007; available at: http://fapar.jrc.ec.europa.eu/). This biophysical indicator has been chosen because it reveals the level of

vegetation photosynthetic activity, which signifies the amount, state and health of vegetation canopies. This value is derived from the closure of the energy balance equation inside the canopy and corresponds to the normalized radiant flux in the Photosynthetic Active Radiation (PAR) region of the solar domain. Figure 4 presents the time series of FAPAR that covers January 1998 to December 2005 over the geographical region representing the Sahel defined by [10° N, 20° N, 20° W, 10° E]. Figure 4a displays the FAPAR value using a color scale varying from white, green to red for the value of FAPAR about 0, 0.5 to 1.0 over the Sahel for October 1998. It gives an example of the maximum of observed vegetation. In Fig. 4b FAPAR monthly time-series are displayed after spatial averaging over the Sahelian region. The different colors are for the different years. The strong seasonal cycle is clearly visible and the yearly average variability for the Sahelian region is smaller. This seasonal cycle with a rapid growth of vegetation beginning in May–June reaches a maximum in September. It is hypothesized that the organic acidity measured in Banizoumbou precipitation is related to the vegetation cycle in the Sahel. This vegetation is certainly VOC emitters but no measurements are available to obtain an order of magnitude from this source.

In the Sahelian region, we also think that biomass burning is certainly responsible of a significant part of this organic acidity retrieved in precipitation. For the first time, the contribution of oxalate ions in precipitation with a non negligible VWM of 2 μeq.l^{-1} that is an indicator of the biomass burning source, is measured (Baudet et al, 1990). Moreover, the good correlation measured between K^+ and oxalate (r=0.72) confirms this result. To investigate the potential influence of the biomass burning source in the Sahelian region, historical emissions of biomass burning for the years 1997–2003 obtained from Granier et al. (2007), are analyzed. Black Carbon data, considered as a tracer of combustion, have been monthly averaged on the geographical window defined by [10° N, 20° N, 20° W, 10° E]. Due to the lack of available historical data on satellite burnt areas for the entire period, this inventory uses an alternative method by crossing satellite burnt areas data of the year 2000 (from Global Burnt area 2000 product, see Tansey et al., 2004) and satellite active fire pixels data of the years 1997–

2003 (from World Fire Atlas /ATSR product; see Arino and Rosaz, 1999). Monthly and annual Black Carbon emissions are calculated following the methodology described in Konaré et al. (2007) (Fig. 5). Results emphasize the presence of biomass burning in the "Sahelian window" with a defined seasonal cycle. Dry season takes place from October November to April and the wet season from May to October. BC emissions are non negligible in May and June with emissions from 0.6 to 4 Gg of BC. To compare, the maximum is measured in January with a mean BC emission of 17 Gg over the period 1997–2003.

It is concluded that both biogenic emission from vegetation active at the beginning and in the heart of the wet season; and biomass burning sources at the end of the wet season could explain the organic acidity content of the precipitation chemistry in the Sahelian region. Other tracers for biomass burning such K^+ elevated in 1998 associated to high biomass burning influence the level of organic acidity in rain. In Sect. 5, inter-annual variability is discussed according monthly variations observed in vegetation and BC emissions with the objective to demonstrate how the biogenic or biomass burning emissions of VOC could influence the organic acidity level in rain.

5 Inter-annual variability and trends of rain chemistry in Banizoumbou

VWM concentrations for each element and each year (1994–2005) are given in Table III. Annual VWM concentration and wet deposition fluxes are displayed on Fig. 7a and b. The annual ionic charge is defined as the sum of the VWM for one year. The mean ionic charge in precipitation (1994–2005) is represented on Fig. 7a as a dash line and is equal to 144.1 μeq.l^{-1}. Over the period 1994–2005, the charge varies from a minimum of 111.9 μeq.l^{-1} in 1999 to a maximum of 158.5 μeq.l^{-1} in 2001. The fluctuation of the ionic charge in precipitation on the eleven year period is about ±10%, except for 1999 (−22%).

The mean pH is not highly fluctuating from year to year with a maximum deviation of ±0.1. It has been also noticed that from one year to the next one, the dominant ions

are the same over the 11 period of rainfall collected at Banizoumbou. The inter-annual variations around the mean (1994–2005), calculated for groups of elements representative of the different source identified previously (Sect. 4), are analyzed. The Na^+, Cl^- and $ssMg^{2+}$ VWM range from 6.2 to 12.6 $\mu eq.l^{-1}$, from 5.4 to 12.2 $\mu eq.l^{-1}$ and from 1.4 to 2.9 $\mu eq.l^{-1}$, respectively. These co-fluctuations have the same pattern. The mean variation for the marine source is ±5% with a maximum deviation ±20%. Mean deviation for the terrigeneous contribution including $nssCa^{2+}$, $nssMg^{2+}$ and $nssSO_4^{2-}$ is ±3%. Variation for $nssK^+$ is around ±9%. Maximum deviations around the annual VWM for the terrigenous contribution are comprised between ±15% and ±20%. Concerning the nitrogenous group formed by NH_4^+ and NO_3^- and the organic component with formate and acetate, the same result is observed. Variations around the mean for the nitrogenous and the organic contribution part are maximum and equal to ±5%. However, the yearly deviations for formate and acetate present a higher variability with maximum fluctuations equal to ±20% and ±30%, respectively.

The total ionic content of the precipitation is function of the amplitude of the main sources of atmospheric gases and particles and the rainfall regime and the associated annual total rainfall at the studied site. The analysis of interannual variability reflects clearly the potential variation of the intensity of atmospheric sources associated to a second important factor, i.e. the variation of the annual rainwater depth. The amount of water determines the scavenging of the different atmospheric chemical compound and directly acts as a dilution factor. The analysis of rainfall in the Sahel shows a strong spatial and temporal variability of the same order of magnitude that we found for chemical composition of precipitation (Balme et al., 2006). Another important result is the discrete aspect of the Sahelian rainfall. This process directly affects rain chemistry content and wet deposition fluxes of nutrients. The weight of each process is somewhat difficult to estimate.

Figure 7 displays the calculation of monthly VWM for each species from June to October for the time series 1996–2005. This figure shows the main processes that lead to the chemical load measured in precipitation. The main pattern shows that the first rainy

month defined by June and the last month October, of the wet season have the highest monthly VWM. This is a trend confirmed over our long term precipitation chemistry. It indicates that the beginning of the rainy season allow the scavenging of an important load of atmospheric chemical compounds. During the heart of the wet season, monthly VWM concentrations are reduced, and higher VWM are found at the end of the season. This result indicates that the atmosphere reloads itself, particularly at the end of the rainy season when rainfall events are more discrete. This process is sometimes very efficient and gave a VWM amplitude as large as what is measured during June. In this context, 1998 has a different pattern and presents a regular decrease of monthly VWM from June to October (Fig. 7). However, the June VWM 1998 is found to be the highest of all the database. The atmosphere at the beginning of the 1998 wet season is particularly loaded with organic acids. FAPAR values shows that 1998 vegetation productivity is in the upper range and the biomass burning source presents the highest annual emission (108 Gg BC, mean 82 Gg BC) (Figs. 4 and 5). Active biomass burning activity during May and June of 1998 is noted. Other tracers of biomass burning such K^+ higher in 1998 confirms this result (VWM=9.1 μeq.l^{-1}).

Rainfall in 2002 and 2003 present negative anomalies with registered deficits around 20% compared to mean. Nevertheless, both years present an ionic charge of 8 and 9% higher than the mean. The organic acidity measured in 2002 is the highest for all the datasets and cannot be explained by the low measured FAPAR index associated to a low annual BC emissions. However, Fig. 5 shows that biomass burning in 2002 is particularly important in the Sahelian region at the beginning of the wet season (June) and present until July with BC emissions four times higher than the mean in July (0.4 Gg BC).

The mean Wet Deposition calculated for all the database is 60.1 mmol.m^{-2}.yr^{-1}(Fig. 7b). The fluctuation of the wet deposition in the dry savanna of Banizoumbou for the period (1994–2005) is ±25%. Around this mean value, the WD varies from a minimum of 44.4 mmol.m^{-2}.yr^{-1} in 2000 to a maximum of 81.0 mmol.m^{-2}.yr^{-1} in 1998 (+35%). These two extreme values correspond to extreme

ACPD
8, 5761–5812, 2008

years with positive rainfall anomalies in 1998 and with negative rainfall anomalies in 2000. Wet deposition fluxes are directly correlated to both the annual rainfall amount and the chemical content measured in precipitation. At the Banizoumbou site it has been possible to determine the mean annual chemical characteristics of precipitation for the 11 yr under study. Thus, it can be said that wet deposition is mainly influenced by the annual total rainfall. One can observe that the two rainiest years 1994 and 1998 suffer the higher annual wet deposition. The input of nutrients to the ecosystems removed by wet deposition can be perturbed and diminished if severe drought in arid and semi arid ecosystems persist as in Sahel.

To compare our long term measurements study in Niger (natural dry savanna), we see that in developed countries such as Central and Western Europe (Puxbaum et al., 2002), in North America (Likens et al., 2001), in Central Austria (Puxbaum et al., 2002) and in Brazil (Fornaro et al., 2006), long term precipitation chemistry trends are mainly controlled by reduction on the sulfur and nitrate-nitrogen emissions. The main result of these long term studies shows a decrease of the free acidity reflecting a gradual decrease of atmospheric SO_2 concentrations according to sulfate reduction decisions. The deposition loads, thus present a trend dependant on emission strength.

This study over the Sahelian region is unique for its long-term monitoring of rainfall chemistry. Results are different from those found in developed countries. The inter annual variability of the annual rainfall VWM concentrations shows that the source input over the period 1994–2005 present a natural variability from one year to the next. The observed variability around ±25% is of the same order of magnitude than the rainfall regime variability measured in the sahelian region. As such, rainfall chemistry content appears to be strongly influenced by the intensity (liquid water content) and the temporal repartition of rainy events (Fig. 7). On the other hand, wet deposition, influenced by the atmospheric charge in chemical compounds and the annual total rainwater is more variable. In the Sahelian region, it presents a trend directly driven by the annual rainfall.

6 Comparison of rainwater chemistry in Niger to other sites: focus on the transect dry savanna-wet savanna and forest in West/Central Africa

In the IDAF framework, long-term measurements of precipitation chemistry characteristics for two great West/Central african ecosystems have been recently established. The site of Zoétélé in the equatorial forest of Cameroon has been studied from 1998 to 2000 and the humid savanna of Lamto in Côte d'Ivoire from 1996 to 2002 (Sigha et al, 2003; Yoboue et al., 2005). Results for the ecosystems transect: i.e., dry savanna-wet savanna and forest are displayed in Fig. 8 a and b. The first result is to compare the total chemical charge of the precipitation (Fig. 8a). A strong gradient from 143.7, 100.2 and 86.6 μeq.l^{-1} at Banizoumbou, Lamto and Zoétélé, is observed, respectively. To study the chemical composition of rain along the transect, we group the different ionic species for each site according their characteristics of atmospheric sources identified in the mean rainfall composition (Table 6).

The marine contribution mainly represented by sodium and chloride is comparable in the dry savanna of Niger and the wet savanna of Côte d'Ivoire, even if Lamto is located at 120 km of the coast and Banizoumbou to about 1000 km. For Zoétélé in Cameroon, relatively close to the coast (200 km), the marine contribution is very low and has been attributed to a discharge in marine elements caused by orographic rains for air masses coming from the ocean. Generally, in all the african ecosystems, the marine contribution is low and estimated to represent 10% to 13% of the rain chemistry. We have discussed in Sect. 4 the high contribution of the nitrogenous compounds in all the ecosystems, higher in the dry savanna than in wet savanna or forest. This result is confirmed by measurements performed in Mali (Table 5). The contribution to the total chemical content of rain is however estimated to be quite comparable in all the ecosystems and equal to 21% to 25% of the total. The third chemical component identified in the rain is the organic component. Indeed, the organic component has been found as important in the dry savanna than in the other ecosystems. This result is new and can be somewhat surprising. It is thought that vegetation and soils plays an impor-

ACPD
8, 5761–5812, 2008

tant role in semi arid and arid ecosystems with a seasonal cycle well marked (sparse measurements exist on natural emissions from these ecosystems). The dry savanna is certainly less impacted by the biomass burning source and it explains a lower contribution in organic acidity with 9%, compared to the wet savanna and the forest with 17% and 14%, respectively. When the H^+ contribution is analyzed, a strong positive gradient from the dry savanna to the forest is found. The free acidity attributed to H^+ represent 15% of the total chemical composition of the rain in the forested ecosystem. Similar results are obtained in the Amazonian forested ecosystems (Williams et al., 1997; Lara et al., 2001). On the african continent, this study along the transect shows that the potential acidity coming from the nitrogen oxides is equivalent on all the ecosystems. The organic acidity has a gradient from the dry savanna to the forest, but a higher contribution from the wet savanna compared to the forest is noticed. The strongest contribution observed along the transect concern the terrigeneous contribution. The main ion is calcium with concentrations varying from 27.3 μeq.l^{-1} in dry savanna, to 9.5 in wet savanna and 8.9 μeq.l^{-1} in forest. It exists a negative gradient of the major terrigenous species concentrations along the transect dry savanna-wet savanna-forest from north to south of West Africa in relation with source region of dust and their potential transport. This gradient affects the acidity of precipitation along the transect of ecosystems by governing the concentrations of potential neutralizing agents.

To explain the acidity gradient, it is important to analyze key processes in charge of the neutralization of the free acidity. Recent studies in heterogeneous chemistry processes represented by the potential interactions between gases, water and particles have been published: i.e., in the Pacific (Prospero et al., 1995), for the wet savanna of Africa (Yoboué et al., 2005), for Asian aerosol (Carmichaël et al., 1996, 1997), or in India (Kulshrestha, 2003, 2005). In Africa, an original study in the Sahelian region has been conducted through IDAF field measurements and SCAPE modeling simulations (Galy and Modi, 1998; Galy et al., 2001, 2003). Considering the importance of heterogeneous process in the tropical chemistry, it has been decided to recalculate from the measurements made at Banizoumbou over the period 1994–2005, the estimation

of the gaseous and particle phase contribution to the chemical content of the precipitation. To investigate the relative contribution of particles and gases in rainwater, Yoboué et al. (2005) have proposed a calculation of PCrain for the relative particle contribution and GCrain for the gaseous one. The non-volatile cations Ca^{2+}, Na^{+}, Mg^{2+} and K^{+} are considered as representative of the mineral particle phase. In order to apply the neutrality principle, the sum of the cations is equilibrated into an equivalent sum of anions. At the Banizoumbou site, the mean relative contribution in rainwater is 70% fro particles and 30% for gases (1994–2005). Using the same concept, identical computation was made for the two other ecosystems using mean characteristics presented in Table 5. For the wet savanna of Lamto, we obtain a particulate contribution of 42% and a gaseous contribution of 58% for gases, and in the forest of Zoétélé 50% for particulate phase and 50% for the gas phase.

To discuss about atmospheric wet deposition fluxes. Figure 8b displays the wet deposition fluxes of each species along the transect of ecosystems. A clear negative gradient of the global load in precipitation from the dry savanna to the forest (VWM in $\mu eq.l^{-1}$) is identified (Fig. 8a). To the opposite, the wet deposition fluxes is driven by the strong rainfall gradient along the ecosystems transect: with 495.1 mm in the dry savanna of Banizoumbou (Niger), 1204 mm in the wet savanna of Lamto (Côte d'Ivoire) and 2029 mm in the forested ecosystem of Zoétélé (Cameroon). Thus, the wet deposition fluxes is more than two times higher in the forest than in the dry savanna. The total mean annual wet deposition is estimated to be equal to 60.0 $mmol.m^{-2}.yr^{-1}$ in Banizoumbou, 108.6 $mmol.m^{-2}.yr^{-1}$ in Lamto and 162.9 $mmol.m^{-2}.yr^{-1}$ in Zoétélé.

7 Conclusions

Within the framework of the IDAF monitoring network, long-term measurements of precipitation chemistry carried out in a rural area of the Sahelian region of Niger (Banizoumbou), 1994 to 2005, are analyzed for the first time. Rainwater chemistry in Banizoumbou, a representative site for the african semiarid savanna ecosystem, was con-

trolled by soil dust emissions associated to a high terrigeneous contribution. Calcium and carbonates have the higher VWM concentrations and represent about 40% of the total ionic charge of precipitation. The other signatures of atmospheric sources in the Sahelian precipitation are highlighted by the relatively high nitrogen (ammonium and nitrate) and organic ion contents (formic and acetic acids) in precipitation. The nitrogen component is the signature of strong ammonia sources related to animals excreta and strong NO_x emissions from savannas soils rain-induced at the beginning of the wet season. The mean annual NH_3 and NO_2 concentration measured in Banizoumbou (6 ppbv and 2.6 ppbv) and their well marked seasonal cycle confirm this result. Biomass burning and photochemical oxidation of biogenic precursors from vegetation have been identified as potential processes contribution to the formation of organic acids in sahelian precipitation. The organic signature in the dry savanna of banizoumbou is comparable to the measured level in the wet savanna or in the forest. The monsoon air mass coming from the Guinean golf, rich in sea salt aerosols, influence the site of Banizoumbou, and explain the marine signature in the collected precipitation samples. For the Sahelian region, we measured a low acidity in precipitation (pH=5.64). Precipitations present a high buffering capacity with high VWM concentration of NH_4^+ and Ca^{2+}. The interannual variability of the rainwater chemical composition (1994–2005) presents fluctuations between ±5% and ±30% mainly attributed to the variations of sources strength, and to the variations of the annual rainfall depth and its temporal distribution. The wet deposition flux in the Sahelian region fluctuates around ±25% from 1994 to 2005. The study of the African ecosystems transect: dry-savanna-wet savanna-forest indicates a strong negative gradient of the total chemical load of precipitation related to the the terrigeneous contribution gradient. The wet deposition fluxes present an inverse result linked to the strong rainfall gradient along the ecosystems transect.

In the future, it seems necessary to study the chemical composition of the wet deposition in association with the distribution of precipitation to try to understand for example how the numbers of convective systems or rain efficient convective systems affect the

wet deposition chemistry. Spatio-temporal distribution and intermittency of rainfall in the Sahel are key elements to understand hydrological impacts but also wet deposition chemistry in semi-arid regions. Moreover, further studies on sources intensity and dynamic transport of atmospheric compounds transport are needed to understand the interannual variability of rain chemistry and wet deposition. To integrate all these processes, we plan to compare and integrate our experimental results in a modelling study using the ORISAM-RAD-TM4 global model (Guillaume et al., 2007). ORISAM-RAD-TM4 model include a detailed 6-bin dynamic sectional aerosol module. This module will allow to take into account the heterogenous chemistry, key process identified in the control of the rain acidity and associated wet deposition in the Sahelian region. Multi-year simulation will be driven in order to scrutinize the interannual variabilities of wet deposition chemistry over Africa using updated emissions inventories (Granier et al., 2007; Guenther et al., 2006).

Acknowledgement. This work is part of the IDAF (IGAC/DEBITS/AFRICA) project; and was funded by INSU/CNRS "Institut National des Sciences de l'Univers/ Centre National de Recherche Scientifique" and the API "African Monsoon Multidisciplinary Analysis" (AMMA in 2005). We would like to address special thanks to J. P. Lacaux from Medias France who initiated the IDAF program within the IGBP/IGAC framework, and to A. I. Modi from the University of Niamey, who started the IDAF Banizoumbou site in Niger (1994). The authors are grateful to A. Zakou the field technician at the Banizoumbou station and IRD (Institut de Recherche pour le Developpement) in Niamey for logistical support. We thank E. Gardrat and P. Castéra from the "Laboratory of Aerology" in Toulouse who performed all the chemical analysis. We thank Y. M. Tourre from Medias-France for proofreading the manuscript. Based upon a French initiative, AMMA now supported by an international scientific group is currently funded by a large number of agencies, especially from France, the United Kingdom, the United States, and Africa. It has been the beneficiary of a major financial contribution from the European Community's Sixth Framework Research Programme (FP6), see www.amma-international.org.

References

Al-ourabi, H. and Lacaux, J. P.: Dry and wet deposition for nitrogen and sulphur at seven IDAF stations in Tropical Africa, International Global Atmospheric Chemistry (IGAC), Symposium, Crete, Greece, 18–25 September, 2002.

Ambus, P. and Christensen, S.: Measurements of N_2O emission from fertilized grassland : An Analysis of spatial variability, J. Geophys. Res. 99, 16 549–16 555, 1994.

Arino, O. and Rosaz, J. M.: 1997 and 1998 World Fire Atlas using ERS-2 ATSR-2 Data, in Proceedings of conference on Remote Sensing of Joint Fire Science Conference and Workshop, Boise, Idaho, 177–182, 1999.

Avila, A., Queralt-Mitjans, I., and Alarcón, M.: Mineralogical composition of Africa dust delivered by red rains over northeastern Spain, J. Geophys. Res., 102(D18), 21 977–21 996, 1997.

Avila, A., Alarcón, M., and Queralt-Mitjans, I.: The chemical composition of dust transported in red rains-Its contribution to the biogeochemical cycle of a holm oak forest in Catalonia (Spain), Atmos. Environ., 32, 179–191, 1998.

Balme, M., Vischel, T. Lebel, T., Peugoet, C., and Galle, S.: Assessing the water balance in the sahel : Impact of small scale rainfall variability on runoff, Part1: Rainfall variability analysis, J. Hydrol., 331(1–2), 336–348, 2006.

Bates, T., Scholes, M., Doherty, S., and Young, B.(Eds.): IGAC Science Plan & Implementation Strategy IGBP Report 56, The IGAC Science Plan and Implementation Strategy (SP&IS) details the scope and goals of IGAC in it's second decade, The science issues that will be the focus of IGAC are presented, as is an outline of how this is to be achieved, 48 pp., 2006.

Baudet, J. G. R., Lacaux, J. P., Bertrand, J. J., Desalmand, F., Servant, J., and Yoboue, V.: Presence of an atmospheric oxalate source in the intertropical zoneits potential action in the atmosphere, Atmos. Res., 25(5), 465–477, 1990.

Brimblecombe, P., Hara, H., Houle, D., and Novak, M.: Acid Rain – Deposition to Recovery, springer edition, repreinted from water, air and soil pollution: Focus, 7(1–3), p. 420, 2007.

Brocard, D., Lacaux, C., Lacaux, J. P., Kouadio, G., and Yoboué, V.:Emissions from the combustion of biofuels in western Africa, in Global Biomass Burning, edited by: Levine, J. S., MIT Press, 1996.

Chameides, W. L. and Davis, D. D.: Aqueous phase source for formic acid in clouds, Nature, 304, 427–429, 1983.

Carmichael, G. R., Ferm, M., Thongboonchoo, N., Woo, J.-H., Chan, L. Y., Murano, K., Viet, P.

H., Mossberg, C., Bala, R., Boonjawat, J., Upatum, P., Mohan, M., Adhikary, S. P., Shrestha, A. B., Pienaar, J. J., Brunke, E. B., Tai Chen, Tang Jie, Ding Guoan, Leong Chow Peng, Dhiharto, S., Harjanto, H., Jose, A. M., Kimani, W., Kirouane, A., Lacaux, J.-P., Richard, S., Barturen, O., Carrasco Cerda, J., Athayde, A., Tavares, T., Silva Cotrina, J., and Bilici, E.: Measurements of sulfur dioxide, ozone and ammonia concentrations in Asia, Africa, and South America using passive samplers, Atmos. Environ., 37(9–10), 1293–1308 James P. Lodge, Jr. Memorial Issue, Measurement Issues in Atmospheric Chemistry, 2003.

Carmichaël, G. R., Zhang, Y., Chen, L. L., Hong, M. S., and Ueda, H.: Seasonnal variation of aerosol composition at Cheju Island, Korea, Atmos. Environ., 30, 2407–2416, 1996.

Carmichaël, G. R., Hong, M. S., Ueda, H., Chen, L. L., Murano, K., Kang, C., and Shim, S.: Aerosol composition at Cheju Island, Korea, J. Geophys. Res., 102, 6047–6061, 1997.

Crutzen P. J. and Andreae, M. O.: Biomass burning in the tropics : Impact on atmospheric chemistry and biogeochemical cycles, Science, 250, 1669–1678, 1990.

Delmas, R., Loudjani, P., Podaire, A., and Menaut, J. C.: Biomass burning in Africa : An assessment of annually burnt biomass, in Global Biomass Burning : Atmospheric, Climatic and Biospheric Implications, edited by: Levine, J. S., MIT Press, Cambridge, Massachusetts, 126–133, 1991.

Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, Y. J., and Crutzen, P. J.: Role of mineral aerosols as a reactive surface in the global troposphere, J. Geophys. Res, 101, 22 869–22 889, 1996.

Estell, R. E. , Fredrickson, E. L., and Peters, D. P. C.: Journal of Arid Environments, 65(2), 193–195, Special Issue Landscape linkages and cross scale interactions in arid and semiarid ecosystems, 2006.

Ferm, M.: A sensitive Diffusional Sampler. IVL publication B – 1020, Swedish Environmental Research Institute, Box 47086, 402 58 Gotebory, Sweden, 1–1, 1991.

Ferm, M. and Rodhe, H.: Measurements of air concentrations of SO_2, NO_2 and NH_3 at rural sites in Asia, J. Atmos. Chem., 27, 17–29, 1997.

Ferm M., Lindskorg, A., Svanberg, P. A., and Boström, C. A.: New measurement technique for air pollutants (in swedish), Kemish Tidskrift 1, 30–32, 1994.

Fornaro, A. and Gutz, I. G. R.: Wet deposition and related atmospheric chemistry in the Sao Paulo metropolis, Brazil, Part 3: Trends in precipitation chemistry during 1983–2003, 2006.

Galloway, J. N., Likens, G. E., Keene, W. C., and Miller, J. M.: Precipitation in remote areas of the world, J. Geophys. Res., 87, 8771–8786, 1986.

Galy-Lacaux, C. and Modi, A. I.: Precipitation chemistry in the Sahelian Savanna of Niger, Africa. J. Atmos. Chem., 30, 319–334, 1998.
Galy-Lacaux, C., Carmichaël, G. R., Song, C. H., Lacaux, J. P., and Modi, I.: Heterogenous processes involving nitrogenous compounds and Saharan dust inferred from measurements and model calculations Region, J. Geophys. Res., 106, 12 559–12 578, 2001.
Galy-Lacaux, C., Liousse, C., Mallet, M., et al.: LOP and EOP Ground-based Measurements: Characterization of Physico-chemical properties of the african Aerosol., 2nd AMMA international Conference, Karlsruhe, 26–30 November, 2007a.
Gilettm R. W. and Ayers, G. P.: The use of thymol as a biocide in rainwater samples, Atmos. Environ., 254A, 2677–2681, 1991.
Gobron, N., Pinty, B., Verstraete, M. M., and Widlowski, J.-L.: Advanced Vegetation Indices Optimized for Up-Coming Sensors: Design, Performance and Aplications, IEEE Transactions on Geoscience and Remote Sensing, 38, 2489–2505, 2000.
Gobron, N., Pinty, B., Aussedat, O., Chen, J., Cohen, W. B., Fensholt, R., Gond, V., Hummerich, K. F., Lavergne, T., Mélin, F., Privette, J. L., Sandholt, I., Taberner, M., Turner, D. P., Verstraete, M. M., and Widlowski, J.-L.: Evaluation FAPAR products for different canopy radiation transfer regimes: Methodology and results using JRC products derived from SeaWiFS against ground-based estimations, J. Geophys. Res., 111, D13110, doi:10.1029/2005JD006511, 2006.
Gobron, N., Pinty, B., Mélin, F., Taberner, M., Verstraete, M. M., Robustelli, M., and Widlowski, J.-L.: Evaluation of the MERIS/ENVISAT FAPAR product, Adv. Space Res., 39, 105–115, doi:10.1016/j.asr.2006.02.048, 2007.
Goutorbe, J. P., Lebel, T., Tinga, A., Bessemoulin, P., Brouwer, J., Dolman, A.J., Engman, E. T., Gash, J. GC., Hoeffner, M., Kabat, P., Kerr, Y., Monteny, B., Prince, S. D., Said, F., Sellers, P., and Wallace, J. S.: HAPEX-Sahel : A Large-Scale Study of Land- Atmosphere Interactions in the semi-arid Tropics, Annales Geophisicae, 12-53-64, EGS-SPRINGER-VERLAG, 1994.
Gradel, T. E. and Crutzen, P. J.: Atmospheric change : An Earth System Perspective, W. H. Freeman and Company, New York, 446 pp., 1993.
Granier, C., Mieville, A. , Liousse, C., Guillaume, B., Grégoire, J. M., and Mouillot, F: Emissions of gases and aerosols resulting from biomass burning during the 1900–2003 period, EGU General Assembly, Vienna, April 2007.
Guenther, A., Karl, T., Harley, P., Wiedinmyer, P., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and

Aerosols from Nature), Atmos. Chem. Phys., 6, 3181–3210, 2006, http://www.atmos-chem-phys.net/6/3181/2006/.
Guillaume, B., Liousse, C., Rosset, R., Cachier, H., Bessagnet, B., Velthoven, P. V. and Poisson, N.: ORISAM-TM4 : Global modelling of internally mixed size-resolved inorganic/organic aerosols with a focus on carbonaceous components, Tellus B, 59, 283–302, 2007.
Herut, B., Starinsky, A., Katz, A., and Rosenfeld, D.: Relationship between the acidity and chemical composition of rainwater and climatological conditions along a transition zone between large deserts and Mediterranean climate, Israel, Atmos. Environ, 34, 1281–1292, 2000.
Hu, G. P., Balasubramanian, R., and Wu, C. D.: Chemical characterization of rainwater at Singapore, Chemosphere 51, 747–755, 2003.
Hultberg, H. and Ferm, M.: Temporal changes and fluxes of sulphur and calcium in wet and dry deposition, internal circulation as well as in run-off and soil in a forest at Gardsjön, Sweden, Biogeochemistry, 68, 355–363, 2004.
IGAC newsletter no. 27, DEBITS special issue, IGACtivities Newsletter, 2003.
Jaeglé, L., Martin, R. V., Chance, K., Steinberger, L., Kurosu, T. P., Jacb, D. J., Modi, A. I., Yoboué, V., Sigha-Nkandjou, L., and Galy-Lacaux, C.: Satellite mapping of rain-induced nitric oxide emissions form soils, J. Geophys. Res., 109, D21310, doi:10.1029/2004JD004787, 2004.
Jarlan, L., Tourre, Y. M., Mougin, E., Philippon, N., and Mazzega, P.: Dominant patterns of AVHRR NDVI interannual variability over the Sahel and linkages with key climate signals (1982–2003), Geophys. Res. Lett., 32, L04701, doi:10.1029/2004GL021841, 2005.
Kaufman, Y. J., Koren, I., Remer, L. A., Tanre, D., Ginoux, P., and Fan, S.: Dust transport and deposition observed from the Terra-Moderate Resolution Imaging Spectroradiometer (MODIS) spacecraft over the Atlantic OceanDust transport and deposition observed from the Terra-Moderate Resolution Imaging Spectroradiometer (MODIS) space, J. Geophys. Res., 110, D10S12, doi:10.1029/2003JD004436, 2005.
Keene, W. C., Pszenny, A. A., Galloway, J. N., and Hartley, M. E.: Sea-salt corrections and interpretation of constituent ratios in marine precipitation, J. Geophys. Res., 91, 6647–6658, 1986.
Konaré, A., Liousse, C., Guillaume, B., Solmon, F., and Rosset, R.: Sensitivity analysis on BC and OCp emission inventories in Africa: regional climate modeling vs. measurements, Atmos. Chem. Phys. Discuss., accepted, 2007.

Kulshrestha, U. C., Kulshrestha, M. J., Sekar, R., Sastry, G. S. R., and Vairamani, M.: Chemical characteristics of rainwater at an urban site of south-central India, Atmos. Environ., 30, 4149–4154, 2003.

Kulshrestha, U. C., Granat, L., Engardt, M., and Rodhe, H.: Review of precipitation monitoring studies in India-a search for region patterns, Atmos. Environ., 39, 7403–7419, 2005.

Lacaux, J. P.: Wet depositions in the tropics, Chapter 2 "Biosphere Atmosphere Interactions", Part 2.7: 53–55, An Integration and Synthesis of a Decade of Tropospheric Chemistry Research, Series: Global Change – The IGBP Series , edited by: Brasseur, G. P., Prinn, R. G., Pszenny, A. A. P., XIV, 300 pp. 131 illus., Hardcover, 2003.

Lacaux, J. P., Tathy, J. P., and Sigha, L.: Acid wet deposition in the tropics: two case studies using DEBITS measurements, IGACtivities Newsletter of the International Global Atmospheric Chemistry Project, DEBITS Special Issue Nr. 2, 2003.

Lara, L. B. L. S., Artaxo, P., Martitinelli, R. L., Victoria, R. L., Camargo, P. B., Krushe, A., Ayers, G. P., Ferraz, E. S. B., and Ballester, M. V.: Chemical composition of rainwater and anthropogenic influences in the Piracicaba River Basin, Southeast Brazil, Atmos. Environ., 35, 4937–4945, 2001.

Le Barbé, L., Lebel, T., and Tapsoba, D.: Rainfall Variability in West Africa during the Years 1950–90, J. Climate, 15, 187–202, 2002.

Lebel, T., Parker, D. J., Bourles, B., Flamant, C., Marticorena, B., Peugeot, C., Gaye, A., Haywood, J., Mougin, E., Polcher, J., Redelsperger, J.-L., and Thorncroft, C.D.: The AMMA field campaigns: Multiscale and multidisciplinary observations in the West african region, B. Am. Meteorol. Soc., 88(3), 311–320, 2007.

Lebel, T., Sauvageot, H., Hoepffner, M., Desbois, M., Guillot, B., and Hubert, P.: Rainfall estimation in the Sahel : the EPSAT-Niger experiment, Hydrol. Sci. J., 37, 201–215, 1992.

Lebel, T., Diedhiou, A., and Laurent, H.: Seasonal cycle and interannual variability of the Sahelian rainfall hyydrological scales, J. Geophys. Res., 108(D8), 8389, doi:10.1029/2001JD00158, 2003.

Levine, J. S., Winstead, L. E., Parsons, D. A. B., Scholes, M. C., Scholes, R. J., Cofers III, W.R., Cahoon Jr., D. R., and Sebacher, D. I.: Biogenic soil emissions of nitric oxide (NO) and nitrous oxide (N_2O) from savanna in South Africa, J. Geophys. Res., 101, 23 089–23 697, 1996.

Likens G. E., Butler T. J., and Buso, D. C.: Long- and short-term changes in sulfate deposition: Effects of the 1990 Clean Air Act Amendments, Biogeochemistry, 52(1), 1–11, 2001.

Löye-Pilot, M. D., Martin, J. M., and Morelli, J.: Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean, Nature, 321, 427–428, 1986.
Mamane, Y. and Gottlieb, J.: Ten years of precipitation in Haifa, Israel. Water, Air and Soil pollution, 82, 548–558, 1995.
Martiny, N., Richard, Y., and Camberlin, P.: Interannual persistence effects in vegetation dynamics of semi-arid Africa, Geophys. Res. Lett., 32, L24403, doi:10. 1029/2005GL024634, 2005.
Marufu, L., Dentener, F., Lelieveld, J., Andreas, M. O., and Helas, G.: Photochemistry of the african troposphere: Influence of biomass-burning emissions, J. Geophys. Res., 105, 14 513–14 530, 2000.
Matson, P. A., Vitousek, P. M., and Schimel, D. S.: Regional extrapolation of trace gas flux based on soils and ecosystems, in : Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, edited by: Schimel, D. S. and Andreae , M. O., John Wiley and Sons, New York, 97–108, 1989.
Mayaux, P., Bartholomé, E., Fritz, S., and Belward, A. S.: A new land-cover map of Africa for the year 2000, J. Biogeography, 31, 861–877, 2004.
Messager, C., Gallée, H., and Brasseur, O.: Precipitation sensitivity to regional SST in a regional climate simulation during the West african monsoon for two dry years, Clim. Dynam., 22, 249–266, 2004.
Modi, A. I., Lacaux, J. P., Labroue, L., and Baudet, J. G. R.: Chimie des aérosols et des pluies dans la savane semi-aride du Niger pendant la saison humide 1989, Sécheresse, 6, 331–335, 1995.
Moulin, C. and Chiapello, I.: Impact of human-induced desertification on the intensification of Sahel dust emission and export over the last decades, Geophys. Res. Lett., 33(18), L18808, doi:10.1029/2006GL025923, 2006.
Mphepya, J. N., Pienaar, J. J., Galy-Lacaux, C., Held, G., and Turner, C. R.: Precipitation Chemistry in Semi-Arid Areas of Southern Africa : A Case Study of a Rural and an industrial Site, J. Atmos. Chem., 47, 1–24, 2004.
Mphepya, J. N., Galy-Lacaux, C., Lacaux, J. P., Held, G., and Pienaar, J. J.: Precipitation Chemistry and Wet Deposition in Kruger National Park, South Africa, J. Atmos., 53 , 169–183, 2006.
Norman, M., Das, S. N., Pillai, A. G., Granat, L., and Rodhe, H.: Influence of air mass trajectories on the chemical composition of precipitation in India, Atmos. Environ., 35, 4223–4235,

2001.
Otter, L. and Scholes, M.: Biogenic fluxes of carbon and nitrogen in arid and semi-arid ecsystems, Geophysical research Abstracts, 7, 09593, SRedf-ID: 1607-7962/gra/EGU-A-09593, 2005.
Parsons, D. A. B., Scholes, M. C., Scholes, R. J., and Levine, J. S.: Biogenic NO emissions from savanna soils as a function of fire regime, soil type, soil nitrogen and water status, J. Geophys. Res., 101, 23 683–23 688, 1996.
Pienaar, J. J.: Proposal of a new IGAC II task: DEBITS II (Deposition of Biogeochemically Important Trace Species), available at: http://www.igac.noaa.gov/DEBITS.php, 2005.
Puxbaum, H., Smeonov, V., Kalina, M. F., Tsakovski, S., Loffer, H., Heimburger, G., Biel, P., Weber, A. , and Damm, A.: Long term assessment of the wet deposition precipitation chemistry in Austria (1984–1999), Chemosphere, 48, 733–747, 2002.
Prospero, J. M., Schmitt R., Cuevas E., Savoie, D., Graustein, W., Turkenian, K., Volz-Thomas, A., Oltmans, S., Levy, H., and Diaz, A.: Temporal variability of ozone and aerosols in the free troposphere over the eastern North atlantic, Geophys. Res. Lett., 22, 2925–2928, 1995.
Pulido-Villena, E., Reche, I., and Morales-Baquero, R.: Significance of atmospheric inputs of calcium over the southwestern Mediterranean region : High mountain lakes as tools for detection, Global Biogeochem. Cy., 20, GB2012, doi:10. 1029/2005GB002662, 2006.
Rayanaut, C.: Societeis and Nature in the Sahel: Ecological diversity and social dynamics, Global Environ. Chang., 11, 9–18, 2001.
Sanhueza, E. and Andreae, M. O.: Emission of formic and acetic acids from tropical savanna Soils, Geophys. Res. Lett., 18, 1707–1710, 1991.
Satsangi, G. S., Lakhani, A., Khare, P., Singh, S. P., Kumari, K. M., and Srivastava, S. S. : Composition of rain water at a semid-arid rural site in India, Atmos. Environ., 32, 3783–3793, 1998.
Schlesinger, W. H., Gray, J. T., and Gilliam, F. S.: Atmospheric deposition processes and their importance as sources of nutrients in a chaparral ecosystem of Southern California, Water Resour. Res., 18, 623–629, 1982.
Schlesinger, W. H. and Hartley, A. E.: A global budget for atmospheric NH_3, Biogeochemistry, 15, 191–211, 1992.
Serça, D., Delmas, R., Le Roux, X., Parsons, D. A. B., Scholes, M. C., Abbadie, L., Lensi, R., and Labroue, L : Comparison of nitrogen monoxide emissions from african tropical ecosystems, Global Biogeochem. Cy., 12, 637–651, 1998.

Sigha-Nkamdjou, L., Galy-Lacaux, C., Pont, V., Richard, S., Sighoumnou, D., and Lacaux, J. P.: Rainwater chemistry and wet deposition over the equatorial forested ecosystem of Zoétélé (Cameroon), J. Atmos. Chem., 46, 173–198, 2003.

Talbot, R. W., Andreae, M. O., Berresheim, H., Jacobs, D. J., and Beecher, K. M.: Sources and sinks of formic, acetic and pyruvic acids over central Amazonia, 2, Wet season, J. Geophys. Res., 95, 16 799–16 811, 1990.

Talbot, R. W., Beecher, K. M., Hariss, R. C., and Cofers III, W. R.: Atmospheric geochemistry of formic and acetic acids at a mid-latitude temperate site, J. Geophys. Res., 93, 1638–1652, 1988.

Tansey, K., Grégoire, J.-M., Binaghi, E., Boschetti, L., Brivio, P. A., Ershov, D., Flasse, S., Fraser, R., Graetz, D., Maggi, M, Peduzzi, P., Pereira, J., Silva, J., Sousa, A., and Stroppiana, D.: A global inventory of burned areas at 1 km resolution for the year 2000 derived from SPOT VEGETATION data, J. Geophys. Res., 109, D14S03, doi:10.1029/2003JD003598, 2004.

Turner, C. R., Wells, R. B., and Olbrich, K. A.: Deposition chemistry in South Africa, in Air Pollution and its Impacts on the South african Highveld, edited by Held, G., Gore, B. J., Surridge, A. D., Tosen, G. R., Walmsley, C. R, and R. D., Environmtal Scientific Association, Cleveland, 80–85, 1996.

Whelpdale, D. M., Summer, P. W., and Sanhueza, E.: Global acid deposition assessment, World Meteorological Organization, Global Atmosphere Watch, edited by Whelpdale, D. M. and Kaiser, M. S., 106, 1996.

Williams, M. R., Fischer, T. M., and Melack, J. M.: Chemical composition and deposition of rain in the central amazon, Brazil, Atmos. Environ., 31, 207–217, 1997.

WMO Report, Quality Control of the WMO Historial Precipitation Chemistry Dabase At EPA Using the Research Data Management And Quality Control (RDMQ) System, WDCPC No. 1, World Meteorological Organization-Global Atmosphere Watch, Geneva, November 1997.

WMO, Global Atmospheric Watch: Report on passive samplers for atmospheric chemistry measurements and their role in GAW, Geneva, 122, 19 pp., 1997.

Yoboué, V., Galy-Lacaux, C., Lacaux, J. P., and Silué, S.: Rainwater Chemistry and Wet Deposition over the Wet Savanna Ecosystem of Lamto (Côte d'Ivoire), J. Atmos. Chem., 52, 117–141, 2005.

Table 1. Rainwater collection in Banizoumbou (1994–2005): annual rainfall (H) in mm, collected rainfall depth (Hc) in mm and Efficiency Collection (EC) in %.

Year	H	Hc	EC
1994	689.1	640.2	93
1995	455.5	–	–
1996	503.5	384.4	76
1997	489.0	418.5	86
1998	699.2	657.2	94
1999	533.4	525.9	99
2000	407.2	385.5	95
2001	401.8	350.1	87
2002	418.2	384.0	92
2003	518.8	476.0	92
2004	420.5	355.7	85
2005	404.9	372.0	92
Total	5941.1	4949.5	90
Mean	495.1	450.0	

Table 2. Correlation coefficients between ions in rainwater over the eleven years (1994–2005). The "Spearman" method was used with a 1% confidence level.

	H^+	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	NO_3^-	Cl^-	SO_4^{2-}	$HCOO^-$	CH_3OOO^-	$C_2O_4^{2-}$
H^+	1.00											
Na^+		1.00										
NH_4^+		0.55	1.00									
K^+		0.81	0.63	1.00								
Ca^{2+}		0.52	0.62	0.51	1.00							
Mg^{2+}		0.52	0.59	0.66	0.85	1.00						
NO_3^-	0.46	0.50	0.74	0.59	0.75	0.75	1.00					
Cl^-		0.78	0.49	0.74	0.36	0.40	0.45	1.00				
SO_4^{2-}	0.31	0.62	0.61	0.46	0.83	0.72	0.74	0.44	1.00			
$HCOO^-$	0.81		0.64				0.59		0.29	1.00		
CH_3OOO^-	0.57		0.72				0.67		0.50	0.71	1.00	
$C_2O_4^{2-}$	0.33	0.24	0.63	0.72	0.55	0.55	0.71	0.05	0.58	0.57	0.68	1.00

ACPD
8, 5761–5812, 2008

Table 3. Annual Volume Weighted Mean (VMW) concentrations in μeq.l^{-1} measured at Banizoumbou during the period 1994–2005.

	1994	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	1994–2005
H^+	–	2.4	1.9	2.4	–	1.9	–	2.4	1.8	2.0	2.3	2.3
pH	–	5.62	5.72	5.62	–	5.7	–	5.62	5.70	5.70	5.60	5.64
Na^+	8.9	7.7	6.2	6.7	8.3	11.1	12.6	9.6	8.3	11.0	9.7	8.7
K^+	7.6	4.7	3.9	9.1	5.5	5.4	7.2	8.2	8.0	7.9	7.4	7.5
Ca^{2+}	23.6	28.3	34.6	27.2	24.1	25.7	36.3	26.3	23.8	31.9	23.4	27.3
Mg^{2+}	6.0	5.2	7.4	6.8	5.4	8.3	8.4	8.7	6.8	5.8	5.1	6.7
NH_4^+	20.6	12.9	16.0	16.4	18.8	14.3	15.6	19.1	16.5	20.8	20.6	18.1
NO_3^-	12.4	12.1	11.7	12.1	10.3	9.3	15.2	15.2	9.4	12.3	10.2	11.6
Cl^-	9.2	7.4	5.4	8.6	7.8	9.9	10.7	12.2	7.4	11.0	8.7	8.7
SO_4^{2-}	9.6	8.2	8.8	9.0	8.5	10.0	11.6	10.2	10.9	11.6	7.6	9.4
t carbonates	27.3	23.4	21.6	24.1	23.2	26.1	40.9	26.0	37.3	23.9	28.3	28.2
HCOO	–	5.7 (5.4*)	7.8 (7.7*)	8.8 (8.7*)	–	–	–	9.3 (9.1*)	7.9 (7.8*)	8.6 (8.5*)	7.8 (7.7*)	8.1 (8.0*)
CH_3COO	–	3.8 (2.3*)	4.6 (4.2)	5.9 (5.3*)	–	–	–	6.6 (5.7*)	5.9 (5.4*)	8.2 (7.5*)	6.3 (5.7*)	5.9 (5.2*)
C_2H_5COO	–	0.3 (0.2*)	0.3 (0.3)	0.2 (0.1*)	–	–	–	1.2 (1.1*)	–	0.2 (0.2*)	0.3 (0.2*)	0.4 (0.4*)
C_2O_4	–	–	–	1.6 (1.6*)	–	–	–	2 (1.9*)	1.4 (1.4*)	2.6 (2.6*)	2.8 (2.7*)	2.0 (2.0*)

* Dissociated fraction of organic acids are noted in brackets.

ACPD
8, 5761–5812, 2008

Table 4. Comparison of sea water ratios with rain water components at Banizoumbou.

	Cl^- / Na^+	SO_4^{2-} / Na^+	K^+ / Na^+	Ca^{2+} / Na^+	Mg^{2+} / Na^+
Sea water ratios (Keene et al., 1986)	1.16	0.121	0.022	0.044	0.227
Ratios in rain	1.000	1.080	0.862	3.138	0.770
EF	0.9	8.9	39.2	71.3	3.4

Table 5. Annual volume weighted mean concentrations in μeq.l^{-1} and wet deposition in mmol.m^{-2}.yr^{-1} (in parenthesis) for precipitation collected in selected IDAF sites.

Ecosystem	Location	Yearly rainfall*	Reference	pH	H^+	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	NO_3^-	Cl^-	SO_4^{2-}	$HCOO^-$	CH_3COO^-	$C_2O_4^{2-}$
Dry Savanna	Banizoumbou Niger	489.5 (1996)	Galy-Lacaux and Modi, 1998	5.67	2.1 (1.0)	7.7 (3.7)	4.7 (2.3)	12.9 (6.3)	31.2 (7.6)	5.6 (1.4)	12.3 (6.0)	7.4 (3.6)	8.6 (2.1)	4.5 (2.3)	2.7 (1.5)	
		495.1 (1994–2005)	**This work**	**5.64**	**2.3 (1.1)**	**8.7 (4.3)**	**7.5 (3.7)**	**18.1 (9.0)**	**27.3 (6.8)**	**6.7 (1.7)**	**11.6 (5.7)**	**8.7 (4.3)**	**9.4 (2.3)**	**8.0 (4.0)**	**5.2 (2.6)**	**2.0 (0.5)**
	Katibougou Mali	797.1 (1997–2005)	Galy-Lacaux (2007) (pers. com.)	5.44	3.7 (2.8)	6.3 (4.8)	3.7 (2.8)	17.4 (13.4)	28.1 (10.8)	4.5 (1.7)	9.7 (7.4)	6.6 (5.1)	7.1 (2.7)	10.8 (8.1)	5.5 (4.2)	2.4 (1.0)
Semi-arid Savanna	Amersfoort South Africa	755.0 (1986–1999)	J. M. Mphepya et al., (2005)	4.35	44.9 (33.9)	9.3 (7.0)	4.7 (3.5)	22.3 (16.8)	18.7 (7.1)	6.7 (2.5)	25.0 (18.9)	9.8 (7.4)	59.1 (22.3)	6.0 (4.5)	2.0 (1.5)	
	Louis Trichardt South Africa	748.0 (1986–1999)	J. M. Mphepya et al., (2005)	4.91	12.2 (9.1)	9.3 (7.0)	3.8 (2.8)	9.7 (7.3)	12.0 (4.5)	4.1 (1.5)	8.0 (6.0)	10.0 (7.5)	14.5 (5.4)	11.5 (8.6)	4.3 (3.2)	
Wet Savanna	Lamto Côte d'Ivoire	1204.0 (1995–2002)	V. Yoboué et al., (2005)	5.16	6.9 (8.4)	6.3 (7.6)	2.4 (2.9)	17.6 (21.2)	9.5 (5.7)	2.7 (1.6)	7.7 (9.2)	7.1 (8.5)	6.5 (3.9)	11.1 (13.4)	6.0 (7.2)	1.4 (0.8)
Forest	Zoetele Cameroon	2029.0 (1996–2000)	Sigha et al. (2003)	4.92	12.0 (24.3)	4.0 (8.1)	5.0 (10.3)	10.5 (21.4)	8.9 (9.0)	2.4 (2.4)	6.9 (13.8)	4..3 (8.7)	5.1 (4.9)	8.2 (17.4)	3.2 11.1	1.0 (1.1)

* Yearly rainfall in mm, ( ): value of wet deposition.

Table 6. Estimation of the marine, the nitrogenous, the organic, the acidity and the terrigenous contribution to the rain chemical content along a transect of African ecosystem.

	Dry savanna Banizoumbou (1994–2005) This work.	Wet savanna Lamto (1995–2002) Zoétélé (1996–2000)	Forest V. Yoboué et al. (2005) Sigha et al. (2003)
Marine $Na^+ + Cl^-$	12%	13%	10%
Nitrogenous $NH_4^+ + NO_3^-$	21%	25%	21%
Organic $HCOO^- + CH_3COO^- + C_2H_5COO^-$	9%	17%	14%
Terrigenous $Ca^{2+} + Mg^{2+} + SO_4^{2+} + K^+ +$tcarbonates	55%	36%	38%
Acidity H^+	2%	15%	7%

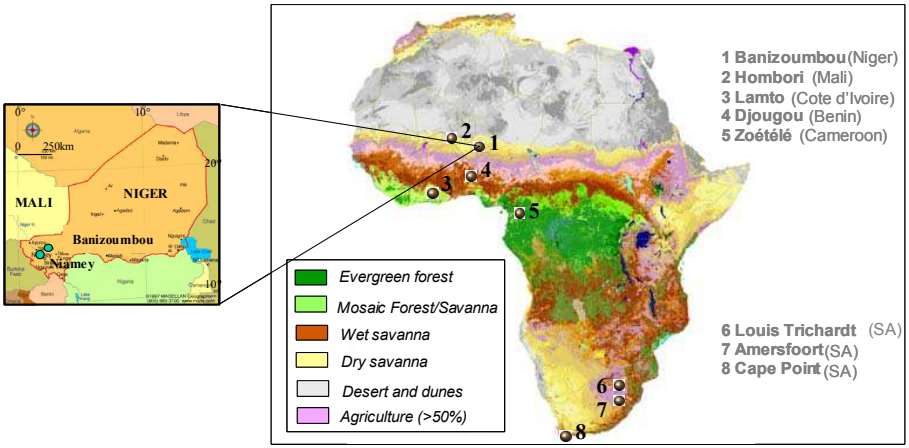

Fig. 1. Vegetation and localization map of the 8 measurement stations of the IDAF network Zoom on the map of Niger with location of the IDAF site of Banizoumbou.

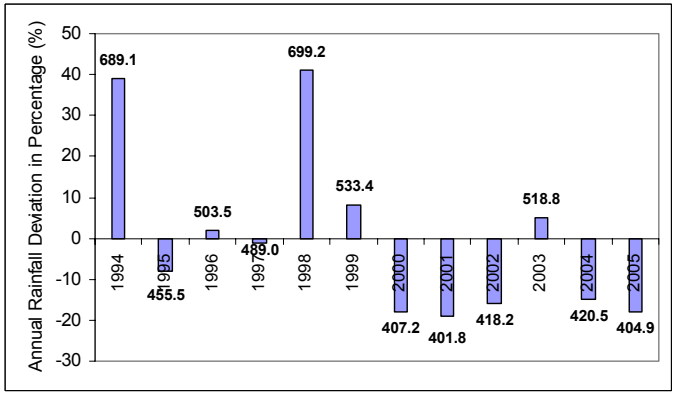

Fig. 2. Inter-annual variability of precipitation at Banizoumbou in %, calculated from the deviation of annual precipitation to the mean annual rainfall for the period 1994–2005 (495.1 mm). Annual rainfall in mm is indicated on the bar.

ACPD
8, 5761–5812, 2008

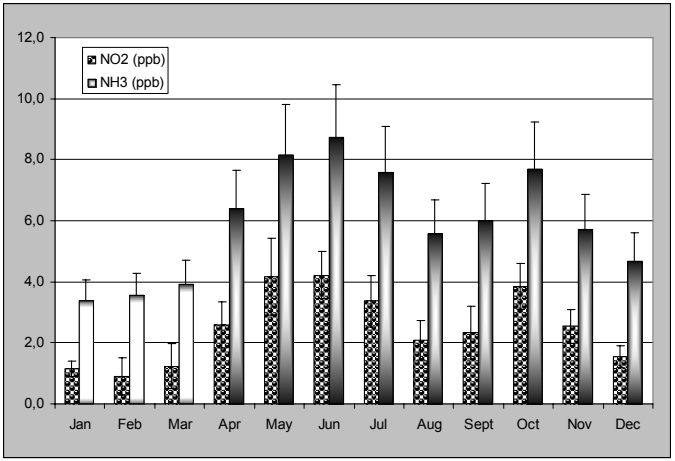

Fig. 3. Mean monthly concentration of NH_3 and NO_2 in ppb at the Banizoumbou site from 1998 to 2004. Vertical bars represent the standard deviation around each monthly mean.

ACPD
8, 5761–5812, 2008

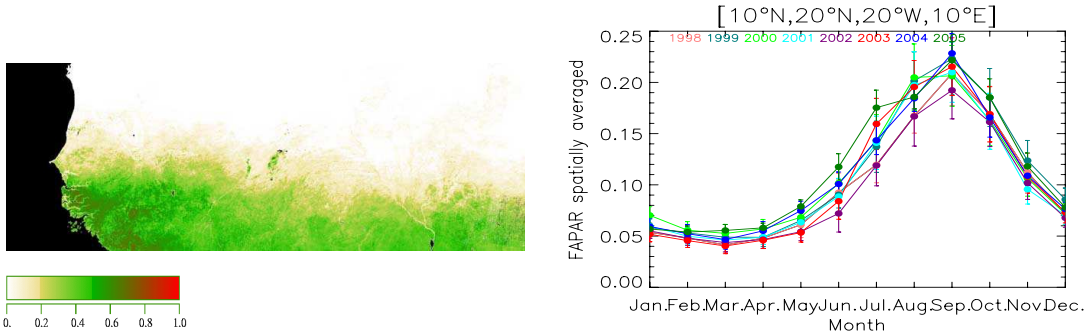

Fig. 4. **(a)** Map of FAPAR for the Sahel region in October 1998. **(b)** Time series of spatially monthly averaged Fractionof Absorbed Photosynthetically Active Radiation (FAPAR) values derived over the Sahel region from 1998 to 2005. The vertical bars indicate the standard deviation, thus indicating the current spatial variability over this geographical window.

ACPD
8, 5761–5812, 2008

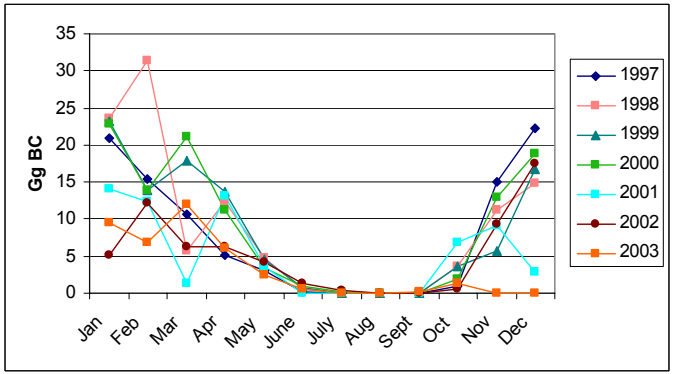

Fig. 5. Monthly Black Carbon (BC) emission in Gg C, as tracer of the biomass burning in the Sahel region defined by [10° N, 20° N, 20° W, 10° E] from 1997 to 2003.

ACPD
8, 5761–5812, 2008

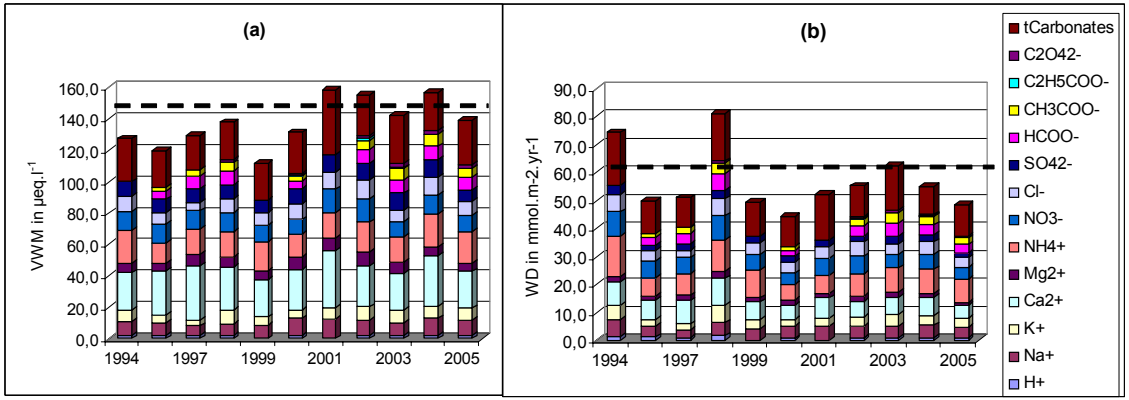

Fig. 6. **(a)** Annual Volume Weighted Mean concentration (μeql^{-1}) in precipitation over the eleven years period (1994–2005) at the dry savanna site of Banizoumbou. **(b)** Annual Wet Deposition fluxes (mmol.m^{-2}yr^{-1}). The horizontal bars indicate the mean VWM and WD calculated from all the database.

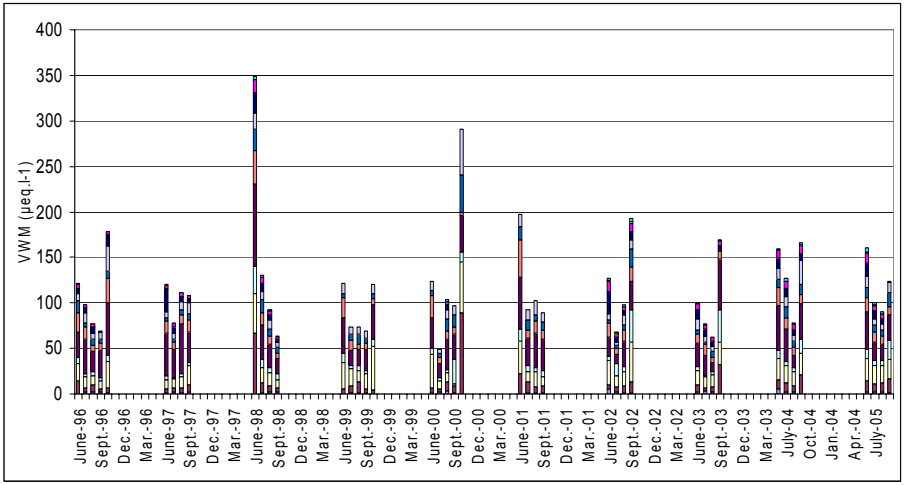

Fig. 7. Monthly total VWM measured in precipitation at Banizoumbou from June to October for the 1998–2005 period.

ACPD
8, 5761–5812, 2008

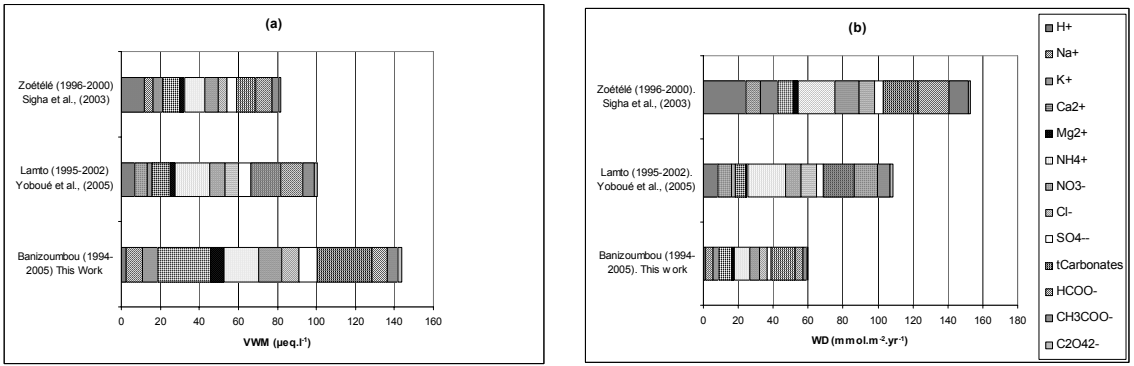

Fig. 8. (a) Annual Volume Weighted Mean concentration (μeq.l^{-1}) representative of the African ecosystems : dry savanna-wet savanna-forest. **(b)** Annual wet deposition fluxes for the ecosystem transect (mmol.m^{-2}yr^{-1}).

ACPD
8, 5761–5812, 2008